CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-2-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) This question paper contains **33** questions. **All** questions are **compulsory**.

(ii) This question paper is divided into **FIVE** sections – Section **A, B, C, D** and **E**.

(iii) **Section A** – questions number **1** to **16** are multiple choice type questions. Each question carries **1** mark.

(iv) **Section B** – questions number **17** to **21** are very short answer type questions. Each question carries **2** marks.

(v) **Section C** – questions number **22** to **28** are short answer type questions. Each question carries **3** marks.

(vi) **Section D** – questions number **29** and **30** are case-based questions. Each question carries **4** marks.

(vii) **Section E** – questions number **31** to **33** are long answer type questions. Each question carries **5** marks.

(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section –A.

(ix) Kindly note that there is a separate question paper for Visually Impaired candidates.

(x) Use of calculator is NOT allowed.

You may use the following values of physical constants wherever necessary :

$c = 3 \times 10^8$ m/s

$h = 6.63 \times 10^{-34}$ J s

$e = 1.6 \times 10^{-19}$ C

$\mu_0 = 4\pi \times 10^{-7}$ T m A^{-1}

$\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 N^{-1} m^{-2}

$\frac{1}{4\pi\varepsilon_0} = 9 \times 10^9$ N m^2 C^{-2}

Mass of electron $(m_e) = 9.1 \times 10^{-31}$ kg.

Mass of neutron $= 1.675 \times 10^{-27}$ kg.

Mass of proton $= 1.673 \times 10^{-27}$ kg.

Avogadro's number $= 6.023 \times 10^{23}$ per gram mole

Boltzmann's constant $= 1.38 \times 10^{-23}$ J K^{-1}

Section A (16 marks)

*Question No. **1** to **16** are Multiple Choice type questions carrying **1** mark each.*

1. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is [1 mark]

(A) 1 F

(B) 3 F

(C) 5 F

(D) 6 F

Correct Answer: (B) 3 F

Solution:

Concept:

- Reduction lowers the oxidation number by gain of electrons. Oxygen has oxidation number -2 in both $\mathrm{MnO_4^-}$ and $\mathrm{MnO_2}$.
- One faraday, F, is the charge carried by one mole of electrons. If one mole of a species gains n moles of electrons, the required charge is $Q = nF$.

Step 1: Determine the electron requirement Let the oxidation number of manganese in $\mathrm{MnO_4^-}$ be x. Then $x + 4(-2) = -1$, so $x = +7$. In $\mathrm{MnO_2}$, $x + 2(-2) = 0$, giving $x = +4$. Each manganese centre therefore gains $7 - 4 = 3$ electrons during the reduction.

Step 2: Convert electrons into charge and check the options One mole of $\mathrm{MnO_4^-}$ contains one mole of manganese centres and requires three moles of electrons. Therefore $Q = 3F$. Option (A), $1F$, supplies only one mole of electrons; option (C), $5F$, corresponds to reduction of manganese from $+7$ to $+2$, a different product; and option (D), $6F$, supplies twice the required charge. Only option (B) matches the stated product $\mathrm{MnO_2}$.

Step 3: Conclusion The required charge is $\boxed{3F}$. Hence, the correct option is (B).

Quick Tip to Solve: First find the manganese oxidation number in the specified product: reduction to $\mathrm{MnO_2}$ needs three electrons, whereas reduction to $\mathrm{Mn^{2+}}$ needs five.

2. Which among the following is a false statement? [1 mark]

(A) Rate of zero order reaction is independent of initial concentration of reactant.

(B) Half-life of a zero order reaction is inversely proportional to the rate constant.

(C) Molecularity of a reaction may be zero.

(D) For a first order reaction, $t_{1/2}$ = 0.693/k.

Correct Answer: (C) Molecularity of a reaction may be zero.

Solution:

Concept:

- Molecularity counts the reacting species in one elementary step and is always a positive integer.

Quick Tip to Solve: Separate the two ideas: order is a rate-law exponent, while molecularity counts species in an elementary step and cannot be zero.

- A zero-order reaction has rate k and half-life $t_{1/2} = [A]_0/(2k)$, where $[A]_0$ is the initial reactant concentration.
- For a first-order reaction, $t_{1/2} = \ln 2/k = 0.693/k$.

Step 1: Check the kinetic statements For zero order, the concentration occurs to power zero in the rate law, so the rate is independent of initial concentration: (A) is true. Its half-life contains k in the denominator, making (B) true at a fixed initial concentration. The first-order half-life expression in (D) is also correct.

Step 2: Test the molecularity statement An elementary reaction requires at least one reacting molecule, atom or ion. Therefore molecularity can be one, two or occasionally three, but cannot be zero. Zero order is possible because order is obtained from the experimentally determined rate law; it must not be confused with molecularity.

Step 3: Conclusion The statement that molecularity may be zero is false. Hence, the correct option is (C).

Quick Tip to Solve: Separate the two ideas: order is a rate-law exponent, while molecularity counts species in an elementary step and cannot be zero.

3. The number of molecules that react with each other in an elementary reaction is a measure of the: [1 mark]

(A) activation energy of the reaction

(B) stoichiometry of the reaction

(C) molecularity of the reaction

(D) order of the reaction

Correct Answer: (C) molecularity of the reaction

Solution:

Concept:

- Molecularity is the number of reacting species participating in a single elementary reaction.
- Order is the sum of concentration exponents in the experimentally determined rate law; activation energy is the energy barrier to reaction.

Step 1: Identify the quantity being counted The question specifies an elementary reaction and counts the molecules that react with each other in that step. One participant gives a unimolecular step and two participants give a bimolecular step. This count is precisely the definition of molecularity.

Step 2: Distinguish the other quantities Activation energy in (A) is an energy, not a molecule count. Stoichiometry in (B) describes reactant and product proportions in a balanced equation and is not the name of this elementary-step count. Order in (D) comes from the rate law. For an elementary step its value may coincide with molecularity, but the definition asked here remains molecularity.

Step 3: Conclusion The number of molecules reacting in an elementary step measures its molecularity. Hence, the correct option is (C).

Quick Tip to Solve: When the wording counts reacting molecules in one elementary step, choose molecularity; rate-law powers indicate order.

4. The element having $[Ar]3d^{10}4s^1$ electronic configuration is [1 mark]

(A) Cu

(B) Zn

(C) Cr

(D) Mn

Correct Answer: (A) Cu

Solution:

Concept:

- A neutral atom's electron count equals its atomic number. The argon core contains 18 electrons.
- Copper has ground-state configuration $[\mathrm{Ar}]\,3d^{10}4s^1$; its filled $3d$ subshell contributes to the stability of this configuration.

Step 1: Count the electrons Add the argon-core electrons to the electrons in the indicated subshells:

$$Z = 18 + 10 + 1 = 29.$$

Atomic number 29 identifies copper, whose chemical symbol is Cu.

Step 2: Compare the remaining elements Zinc has configuration $[\mathrm{Ar}]\,3d^{10}4s^2$, chromium has $[\mathrm{Ar}]\,3d^5 4s^1$, and manganese has $[\mathrm{Ar}]\,3d^5 4s^2$. Thus zinc has an extra $4s$ electron, while chromium and manganese have only five $3d$ electrons. None matches the given arrangement.

Step 3: Conclusion The element is copper, Cu. Hence, the correct option is (A).

Quick Tip to Solve: Add 18 for the argon core to the stated subshell populations; a total of 29 immediately identifies copper.

5. The complex ions $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$ are called [1 mark]

(A) Ionization isomers

(B) Linkage isomers

(C) Co-ordination isomers

(D) Geometrical isomers

Correct Answer: (B) Linkage isomers

Solution:

Concept:

- An ambidentate ligand can coordinate through either of two different donor atoms, one at a time.
- Linkage isomerism occurs when the same ligand binds through different donor atoms in otherwise identical complexes.

Step 1: Identify the donor atoms The nitrite ligand, NO_2^-, is ambidentate. In $[Co(NH_3)_5(NO_2)]^{2+}$ it binds to cobalt through nitrogen (the nitro form). In $[Co(NH_3)_5(ONO)]^{2+}$ it binds through oxygen (the nitrito form). The five ammine ligands and the overall charge remain the same.

Quick Tip to Solve: Recognise the pair NO_2/ONO: nitrogen versus oxygen attachment of the same nitrite ligand signals linkage isomerism.

Step 2: Classify the change The change is in the atom through which nitrite attaches to the same metal centre. There is no exchange with a counter-ion as in ionization isomerism, no exchange between cationic and anionic complex ions as in coordination isomerism, and no change merely in the spatial arrangement as in geometrical isomerism. This is the defining feature of linkage isomers.

Step 3: Conclusion The two complex ions are linkage isomers. Hence, the correct option is (B).

Quick Tip to Solve: Recognise the pair NO_2/ONO: nitrogen versus oxygen attachment of the same nitrite ligand signals linkage isomerism.

6. The diamagnetic species is: [At. No. Co = 27, Fe = 26, Ni = 28] [1 mark]

(A) $[Ni(CN)_4]^{2-}$

(B) $[NiCl_4]^{2-}$

(C) $[Fe(CN)_6]^{3-}$

(D) $[CoF_6]^{3-}$

Correct Answer: (A) $[Ni(CN)_4]^{2-}$

Solution:

Concept:

- A diamagnetic complex has no unpaired electrons; one or more unpaired electrons make it paramagnetic.
- Ligand strength and geometry determine the electron arrangement: CN^- promotes pairing, while Cl^- and F^- are weak-field ligands.

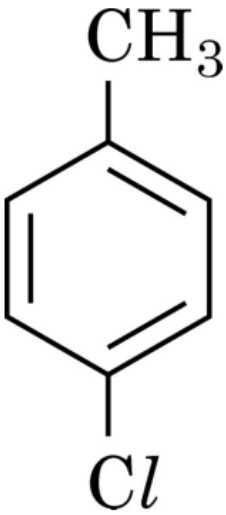
Step 1: Analyse the nickel complexes Both nickel complexes contain Ni^{2+}, which is $3d^8$. In $[Ni(CN)_4]^{2-}$, the strong-field cyanide ligands produce a square-planar dsp^2 complex with all electrons paired. In $[NiCl_4]^{2-}$, the weak-field chloride ligands give a tetrahedral complex with two unpaired electrons.

Step 2: Check the iron and cobalt complexes In $[Fe(CN)_6]^{3-}$, iron is Fe^{3+} with d^5 configuration. Even the low-spin octahedral arrangement t_{2g}^5 has one unpaired electron. In $[CoF_6]^{3-}$, cobalt is Co^{3+} with d^6 configuration; weak-field fluoride gives the high-spin arrangement $t_{2g}^4 e_g^2$, containing four unpaired electrons. Therefore both are paramagnetic.

Step 3: Conclusion Only $[Ni(CN)_4]^{2-}$ has no unpaired electrons and is diamagnetic. Hence, the correct option is (A).

Quick Tip to Solve: Strong-field ligands do not always give diamagnetism: low-spin d^5 still has one unpaired electron. Check the final electron count.

7. Which is the correct IUPAC name for [1 mark]



(A) Methylchlorobenzene

(B) Toluene

(C) 1-Chloro-4-Methylbenzene

(D) 1-Methyl-4-Chlorobenzene

Correct Answer: (C) 1-Chloro-4-Methylbenzene

Solution:

Concept:

- Name a disubstituted benzene by specifying each substituent and its position on the ring.
- Use the lowest set of locants. If the same locant set results from either direction, assign the lower locant to the substituent cited first alphabetically.

Step 1: Read the ring substituents The printed structure has a methyl group, CH_3, and a chlorine atom on opposite carbon atoms of a benzene ring. The groups are in the para relationship, so their locants are 1 and 4 regardless of which group starts the numbering.

Step 2: Resolve the numbering tie Chloro comes before methyl alphabetically, so chlorine receives locant 1 and methyl receives locant 4. The resulting name is 1-chloro-4-methylbenzene. Option (A) omits the positions and cannot identify the displayed isomer; (B), toluene, omits the chlorine entirely. Option (D) reverses the locant assignment and does not follow the alphabetical tie-breaking rule.

Step 3: Conclusion The correct name among the given choices is 1-chloro-4-methylbenzene. Hence, the correct option is (C).

Quick Tip to Solve: For opposite substituents use locants 1,4; when numbering ties, chloro precedes methyl alphabetically and gets locant 1.

8. What will be formed after oxidation reaction of secondary alcohol with chromic anhydride (CrO_3)?

[1 mark]

(A) Aldehyde

(B) Ketone

(C) Carboxylic acid

(D) Ester

Correct Answer: (B) Ketone

Solution:

Concept:

- Secondary alcohols have two carbon groups attached to the carbon bearing the hydroxyl group.
- Oxidation with chromic anhydride, CrO_3, converts the secondary alcohol group into a ketone carbonyl group.

Step 1: Identify the oxidation site The carbon bearing the hydroxyl group in a secondary alcohol has one hydrogen atom. Oxidation removes this hydrogen and the hydrogen of the hydroxyl group, producing a carbon-oxygen double bond while retaining both carbon groups.

Step 2: Compare the possible products The carbonyl carbon therefore remains bonded to two carbon groups, which defines a ketone. For example, $CH_3CH(OH)CH_3 + [O] \longrightarrow CH_3COCH_3 + H_2O$. An aldehyde comes from mild oxidation of a primary alcohol; a carboxylic acid generally arises from further oxidation of that aldehyde. Ester formation requires a different reaction, such as esterification.

Step 3: Conclusion The product is a ketone. Hence, the correct option is (B).

Quick Tip to Solve: Count carbon groups on the alcohol carbon: two carbon groups give a ketone on ordinary oxidation.

9. The conversion of phenol to salicylic acid can be accomplished by

[1 mark]

(A) Reimer-Tiemann reaction

(B) Friedel-Crafts reaction

(C) Kolbe reaction

(D) Coupling reaction

Correct Answer: (C) Kolbe reaction

Solution:

Concept:

- In the Kolbe reaction, sodium phenoxide reacts with carbon dioxide under pressure and on acidification gives salicylic acid.
- Salicylic acid is ortho-hydroxybenzoic acid: a carboxyl group is introduced ortho to the phenolic hydroxyl group.

Step 1: Identify the group introduced The required conversion retains the phenolic hydroxyl group and introduces a $-COOH$ group at the ortho position. Phenol is first converted to sodium phenoxide,

Quick Tip to Solve: Remember the introduced group: Kolbe gives ortho-COOH, whereas Reimer-Tiemann gives ortho-CHO.

which is more reactive toward electrophilic substitution.

Step 2: Match the named reaction Sodium phenoxide reacts with CO_2 at about $400\,K$ under pressure to give sodium salicylate. Acidification gives salicylic acid. Reimer-Tiemann reaction introduces an aldehyde group and gives salicylaldehyde. Friedel-Crafts reaction concerns alkylation or acylation, while coupling with a diazonium salt gives an azo compound; neither is this carboxylation.

Step 3: Conclusion The conversion is accomplished by the Kolbe reaction. Hence, the correct option is (C).

Quick Tip to Solve: Remember the introduced group: Kolbe gives ortho-COOH, whereas Reimer-Tiemann gives ortho-CHO.

10. Which of the following is/are examples of denaturation of protein? [1 mark]

(A) Coagulation of egg white

(B) Curdling of milk

(C) Clotting of blood

(D) Both (A) and (B)

Correct Answer: (D) Both (A) and (B)

Solution:

Concept:

- Denaturation disrupts the secondary and tertiary structures of a protein and causes loss of its native biological activity.
- The primary sequence of amino acids usually remains intact during denaturation. Heat or a change in pH can cause the change.

Step 1: Check egg white and milk Heating an egg causes its proteins to unfold and coagulate, so coagulation of egg white is an example of denaturation. During curdling of milk, the acidic conditions alter protein structure and cause casein to coagulate; this is also a standard example of protein denaturation.

Step 2: Distinguish clotting from denaturation Blood clotting is a regulated biochemical process in which soluble fibrinogen is converted by thrombin into fibrin, forming a network. It is not the standard heat- or acid-induced denaturation example intended here. Thus (A) and (B) each identify a valid example, but neither alone includes both examples; option (D) includes both.

Step 3: Conclusion Both coagulation of egg white and curdling of milk are examples. Hence, the correct option is (D).

Quick Tip to Solve: Link denaturation with heat-coagulated egg white and acid-curdled milk; do not equate every protein clot with denaturation.

11. Nucleotides are joined together by [1 mark]

(A) Glycosidic linkage

(B) Peptide linkage

(C) Hydrogen bonding

(D) Phosphodiester linkage

Correct Answer: (D) Phosphodiester linkage

Solution:

Concept:

- A nucleotide consists of a nitrogenous base, a pentose sugar and a phosphate group.
- Adjacent nucleotides in a nucleic acid chain are connected by covalent phosphodiester bonds, forming the sugar-phosphate backbone.

Step 1: Identify the backbone bond The phosphate group links the $3'$ hydroxyl group of one pentose sugar to the $5'$ position of the next nucleotide. Since the phosphate forms two ester bonds to sugar groups, this connection is called a $3'$-$5'$ phosphodiester linkage.

Step 2: Distinguish the other linkages A glycosidic linkage joins the nitrogenous base to the sugar within a nucleotide; it does not join successive nucleotides. A peptide linkage joins amino acids in proteins. Hydrogen bonds join complementary bases between the two DNA strands, but do not form the covalent backbone of a nucleic acid chain.

Step 3: Conclusion Nucleotides are joined together by phosphodiester linkage. Hence, the correct option is (D).

Quick Tip to Solve: Use backbone versus base pairing: phosphodiester joins a strand, hydrogen bonds hold paired DNA bases together.

12. Scurvy is caused due to deficiency of [1 mark]

(A) Vitamin B1

(B) Vitamin B2

(C) Ascorbic acid

(D) Glutamic acid

Correct Answer: (C) Ascorbic acid

Solution:

Concept:

- Vitamin C is chemically known as ascorbic acid and is a water-soluble vitamin.
- Deficiency of vitamin C causes scurvy, commonly associated with bleeding gums and impaired wound healing.

Step 1: Recall the deficiency-disease pair Ascorbic acid supports normal connective-tissue formation, including collagen formation. When its intake is inadequate, connective tissues become weak and the characteristic deficiency disease is scurvy. Therefore the named chemical vitamin, rather than an

Quick Tip to Solve: Keep the standard pair together: scurvy means vitamin C, whose chemical name is ascorbic acid.

amino acid, must be selected.

Step 2: Eliminate the distractors Vitamin B_1, thiamine, is associated with prevention of beriberi. Vitamin B_2, riboflavin, deficiency is associated with symptoms such as cheilosis rather than scurvy. Glutamic acid is an amino acid and is not vitamin C. Ascorbic acid is the only listed substance whose deficiency produces scurvy.

Step 3: Conclusion Scurvy is caused by deficiency of ascorbic acid, or vitamin C. Hence, the correct option is (C).

Quick Tip to Solve: Keep the standard pair together: scurvy means vitamin C, whose chemical name is ascorbic acid.

13. Assertion (A): In a first order reaction, if the concentration of the reactant is doubled, its half-life is also doubled.

Reason (R): The half-life of a reaction does not depend upon the initial concentration of the reactant in a first order reaction. [1 mark]

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- For a first-order reaction, the integrated rate law is $kt = \ln([A]_0/[A]_t)$, where k is the rate constant.
- At half-life, $[A]_t = [A]_0/2$, giving $t_{1/2} = \ln 2/k = 0.693/k$.

Step 1: Evaluate Assertion (A) Substituting the half-life condition into the integrated equation gives

$$t_{1/2} = \frac{1}{k} \ln \frac{[A]_0}{[A]_0/2} = \frac{\ln 2}{k}.$$

Doubling the initial concentration changes both the initial amount and its half in the same ratio. At the same temperature, the rate constant remains fixed, so the half-life remains unchanged. Assertion (A) is false.

Step 2: Evaluate Reason (R) The half-life expression contains the rate constant but no initial-concentration term. Hence a first-order half-life is independent of the initial reactant concentration, and Reason (R) is true.

Step 3: Assess the logical relationship The reason describes the correct first-order property and directly contradicts the proposed doubling of half-life in the assertion. Options (A) and (B) require both statements to be true, while (C) requires a true assertion and a false reason; none matches the

Quick Tip to Solve: For first order, write 0.693/k immediately: concentration cannot change the half-life when k is fixed.

judgments.

Step 4: Conclusion The assertion is false, but the reason is true. Hence, the correct option is (D).

Quick Tip to Solve: For first order, write 0.693/k immediately: concentration cannot change the half-life when k is fixed.

14. Assertion (A): Cu cannot liberate H_2 on reaction with dilute mineral acids.
Reason (R): Cu has positive electrode potential. [1 mark]

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Solution:

Concept:

- The standard reduction potential of the Cu^{2+}/Cu couple is positive, about $+0.34\,V$, relative to the standard hydrogen electrode.
- A metal liberates H_2 from a dilute non-oxidising acid only when oxidation of the metal coupled with reduction of H^+ is spontaneous.

Step 1: Evaluate Assertion (A) For hydrogen liberation, copper would have to undergo $Cu \longrightarrow Cu^{2+} + 2\,e^-$ while the acid supplies $2\,H^+ + 2\,e^- \longrightarrow H_2$. Copper does not reduce hydrogen ions under these conditions, so it does not liberate hydrogen from dilute mineral acids. Assertion (A) is true. Oxidising acids may dissolve copper, but their oxidising species are reduced instead of producing hydrogen gas.

Step 2: Evaluate Reason (R) The stated positive electrode potential refers to the standard reduction potential of copper. Taking $E^\circ(H^+/H_2) = 0$, the proposed hydrogen-liberating cell has

$$E^\circ_{cell} = 0 - (+0.34) = -0.34\,V.$$

Thus Reason (R) is true.

Step 3: Connect the reason to the assertion The negative cell potential shows that coupling copper oxidation to hydrogen-ion reduction is not spontaneous under standard conditions. The positive copper reduction potential therefore explains why copper cannot displace hydrogen from these acids. The alternatives that deny either statement or deny the explanatory connection do not apply.

Step 4: Conclusion Both Assertion (A) and Reason (R) are true, and Reason (R) correctly explains Assertion (A). Hence, the correct option is (A).

Quick Tip to Solve: To check hydrogen displacement, subtract the metal reduction potential from zero; a negative result rules it out.

15. Assertion (A): Aromatic primary amines cannot be prepared by Gabriel Phthalimide synthesis.
Reason (R): Aryl halides do not undergo nucleophilic substitution reaction with the anion formed by phthalimide. [1 mark]

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Solution:

Concept:

- Gabriel synthesis prepares primary amines by alkylating the phthalimide anion, followed by hydrolysis to release the amine.
- Ordinary aryl halides resist the nucleophilic substitution required in this synthesis; their aryl carbon-halogen bond has partial double-bond character.

Step 1: Assess the assertion The assertion is true. Gabriel phthalimide synthesis is suitable for aliphatic primary amines, but cannot prepare aromatic primary amines such as aniline by the corresponding reaction with an aryl halide.

Step 2: Assess the reason The reason is true. The phthalimide anion acts as a nucleophile. An ordinary aryl halide does not undergo the required substitution with this anion, so the necessary arylated intermediate is not obtained under Gabriel synthesis conditions.

Step 3: Connect the reason to the assertion Failure of the aryl-halide substitution step directly prevents formation of the aromatic primary amine. Thus the reason explains the assertion. Option (B) incorrectly denies this explanation; options (C) and (D) incorrectly judge one of the statements as false.

Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is (A).

Quick Tip to Solve: For Gabriel synthesis, check the halide first: alkyl halides work, whereas ordinary aryl halides cannot undergo the required substitution.

16. Assertion (A): Vitamin D cannot be stored in our body.

Reason (R): Vitamin D is fat soluble vitamin and is not excreted from the body in urine. [1 mark]

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- Vitamins A, D, E and K are fat-soluble and can be stored in the liver and fatty tissues.
- Fat-soluble vitamins are not readily eliminated in urine, unlike most water-soluble vitamins.

Step 1: Assess the assertion The assertion is false. Vitamin D is a fat-soluble vitamin and can be stored in our body, especially in the liver and adipose tissues. The claim that it cannot be stored therefore reverses its actual behaviour.

Step 2: Assess the reason The reason is true in the standard classification of vitamins. Vitamin D is fat soluble and is not excreted from the body in urine in the manner of water-soluble vitamins. Its solubility permits retention in fatty tissues.

Step 3: Choose the statement combination Since A is false and R is true, the combination is option (D). Options (A) and (B) require a true assertion, and option (C) requires a false reason; none matches the two statements. The true reason supports storage rather than the assertion's claim of inability to store.

Step 4: Conclusion Assertion A is false, while Reason R is true. Hence, the correct option is (D).

Quick Tip to Solve: Recall the fat-soluble group A, D, E and K: their storage in fatty tissues immediately disproves the assertion about vitamin D.

Section B (10 marks)

17(A). The rate constant for a zero order reaction A $\rightarrow$ P is 0.0030 mol $L^{-1}s^{-1}$. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M? [2 marks]

Solution:

Concept:

- For a zero-order reaction, the rate of disappearance of the reactant is constant: $-d[A]/dt = k$, where $[A]$ is its concentration and k is the rate constant.
- The integrated rate law is $[A]_t = [A]_0 - kt$, so $t = ([A]_0 - [A]_t)/k$. Here t is elapsed time and subscripts 0 and t denote initial and final concentrations.

Quick Tip to Solve: For a zero-order concentration drop, subtract final from initial concentration and divide directly by k; do not use a logarithm.

Step 1: Calculate the concentration decrease Both concentrations are in molarity, with $1\,\text{M} = 1\,\text{mol L}^{-1}$. Thus

$$[A]_0 - [A]_t = 0.10 - 0.075 = 0.025\,\text{mol L}^{-1}.$$

This is the amount of reactant consumed per litre during the required time interval.

Step 2: Apply the zero-order integrated law Substituting the given rate constant,

$$t = \frac{0.025\,\text{mol L}^{-1}}{0.0030\,\text{mol L}^{-1}\text{s}^{-1}} = 8.33\,\text{s} \approx 8.3\,\text{s}.$$

The concentration units cancel and leave seconds. As a check, multiplying k by $8.33\,\text{s}$ gives the required concentration fall of approximately $0.025\,\text{mol L}^{-1}$. A logarithmic expression is unnecessary because the reaction is zero order.

Step 3: Conclusion The concentration of A falls from $0.10\,\text{M}$ to $0.075\,\text{M}$ in approximately $8.3\,\text{s}$.

Quick Tip to Solve: For a zero-order concentration drop, subtract final from initial concentration and divide directly by k; do not use a logarithm.

OR

17(B). The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if k = 2.5 × 10^{-4} mol L^{-1} s^{-1}? [2 marks]

Solution:

Concept:

- For zero-order decomposition, the disappearance rate of ammonia is $-d[\text{NH}_3]/dt = k$, independent of its concentration.
- Stoichiometry converts the disappearance rate to each product's formation rate: consuming two moles of ammonia produces one mole of nitrogen and three moles of hydrogen.

Step 1: Balance the decomposition and relate the rates The balanced reaction is

$$2\text{NH}_3(\text{g}) \xrightarrow{\text{Pt}} \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}).$$

Consequently,

$$\frac{d[\text{N}_2]}{dt} = \frac{1}{2}\left(-\frac{d[\text{NH}_3]}{dt}\right), \qquad \frac{d[\text{H}_2]}{dt} = \frac{3}{2}\left(-\frac{d[\text{NH}_3]}{dt}\right).$$

The product rates are positive because their concentrations increase.

Step 2: Substitute the zero-order rate constant Here the ammonia disappearance rate equals $k = 2.5 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}$. Therefore,

$$\frac{d[\text{N}_2]}{dt} = \frac{1}{2}(2.5 \times 10^{-4}) = 1.25 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1},$$
$$\frac{d[\text{H}_2]}{dt} = \frac{3}{2}(2.5 \times 10^{-4}) = 3.75 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}.$$

Quick Tip to Solve: Balance ammonia decomposition first: divide its disappearance rate by two for nitrogen, then multiply the nitrogen rate by three for hydrogen.

Hydrogen is produced three times as fast as nitrogen, consistent with the balanced equation.

Step 3: Conclusion The rates of production are $1.25 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}$ for N_2 and $3.75 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}$ for H_2.

Quick Tip to Solve: Balance ammonia decomposition first: divide its disappearance rate by two for nitrogen, then multiply the nitrogen rate by three for hydrogen.

18. Define the following terms:

(a) Pseudo first order reaction

(b) Half-life period of reaction ($t_{1/2}$) [2 marks]

Solution:

Concept:

- Reaction order describes the dependence of the experimentally observed rate on reactant concentrations; a reactant in large excess has an approximately constant concentration.
- The half-life $t_{1/2}$ is defined by the reactant concentration becoming half its initial value, that is, $[A]_{t_{1/2}} = [A]_0/2$.

Step 1: Define a pseudo first-order reaction A reaction whose actual order is higher than one but which behaves kinetically as a first-order reaction because one or more reactants are present in large excess is called a pseudo first-order reaction. For example, ester hydrolysis in excess water has an approximately constant water concentration. If its rate is $k[\text{ester}][H_2O]$, this becomes $k'[\text{ester}]$, where $k' = k[H_2O]$ is effectively constant.

Step 2: Define the half-life period The half-life period of a reaction is the time required for the concentration of a reactant to decrease to one-half of its initial concentration. Thus, if the reactant initially has concentration $[A]_0$, after one half-life its concentration is $[A]_0/2$. This definition applies to all reaction orders; the formula and concentration dependence of the half-life depend on the order. For a first-order reaction, $t_{1/2} = 0.693/k$.

Step 3: Conclusion (a) A pseudo first-order reaction is a higher-order reaction that behaves as first order when other reactants are in large excess. (b) Half-life is the time for a reactant concentration to fall to half its initial value.

Quick Tip to Solve: For pseudo first order, state both large excess and effectively constant concentration; for half-life, state exactly half the initial reactant concentration.

19. Explain the following observations:

(a) Transition elements generally form coloured compounds.

(b) Zinc is not regarded as a transition element. [2 marks]

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its common oxidation states.
- In a ligand field, the five d orbitals split into groups of different energies. An electron can absorb visible light and move between these levels.

Step 1: Explain the colour of transition-metal compounds Most transition-metal ions have partly filled d orbitals. Ligands split these orbitals into different energy levels. When the energy gap corresponds to visible radiation, an electron absorbs a particular wavelength and undergoes a d-d transition. The remaining transmitted or reflected light gives the compound its observed colour. Thus, colour is associated with selective absorption, rather than emission of all visible wavelengths.

Step 2: Apply the definition to zinc Zinc has atomic configuration $[\mathrm{Ar}]\,3d^{10}4s^{2}$. Its common ion, Zn^{2+}, has configuration $[\mathrm{Ar}]\,3d^{10}$. Both the atom and its common ion have a completely filled d subshell. Therefore zinc fails the criterion of an incompletely filled d subshell, although it is located in the d block.

Step 3: Conclusion (a) Transition-element compounds are generally coloured because of visible-light absorption in d-d transitions. (b) Zinc is not a transition element because both Zn and Zn^{2+} have a filled $3d^{10}$ subshell.

Quick Tip to Solve: For zinc, write both Zn and Zn^{2+} configurations; position in the d block alone does not establish transition character.

20. Name the following coordination compounds according to IUPAC norms:

(a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$

(b) $[CrCl_2(en)_2]Cl$ [2 marks]

Solution:

Concept:

- Name ligands alphabetically, ignoring numerical prefixes, followed by the metal and its oxidation state in Roman numerals.
- NH_3 is ammine, H_2O is aqua, Cl^- is chlorido, and en is the neutral bidentate ligand ethane-1,2-diamine.

Step 1: Name the cobalt complex In $[\mathrm{Co}(\mathrm{NH_3})_4(\mathrm{H_2O})\mathrm{Cl}]\mathrm{Cl_2}$, the two outer chloride ions give the complex cation a charge of $+2$. Ammine and aqua are neutral, while the coordinated chlorido ligand has charge -1. If cobalt has oxidation state x, then $x - 1 = +2$, so $x = +3$. The alphabetical sequence is ammine, aqua, chlorido. Four ammine ligands give tetraammine. The cation is therefore tetraammineaquachloridocobalt(III), followed by the counterion chloride.

Quick Tip to Solve: Find the complex charge from the outside chloride ions before calculating the metal oxidation state; both metals here are in oxidation state $+3$.

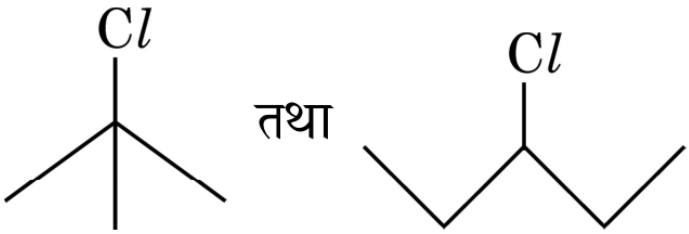
Step 2: Name the chromium complex In $[CrCl_2(en)_2]Cl$, the outside chloride means that the complex has charge $+1$. The two coordinated chlorido ligands contribute -2, and both en ligands are neutral. Thus $x - 2 = +1$, giving chromium oxidation state $+3$. Chlorido precedes ethane-1,2-diamine alphabetically. Use dichlorido for the two chloride ligands and bis(ethane-1,2-diamine) for the two ligands whose name already contains a numerical term. The metal is chromium because the complex is cationic.

Step 3: Conclusion (a) Tetraammineaquachloridocobalt(III) chloride.

(b) Dichloridobis(ethane-1,2-diamine)chromium(III) chloride.

Quick Tip to Solve: Find the complex charge from the outside chloride ions before calculating the metal oxidation state; both metals here are in oxidation state $+3$.

21(a). In the following pair of halogen compounds, which compound undergoes S_N1 reaction faster and why? [1 mark]



Solution:

Concept:

- The slow, rate-determining step in an S_N1 reaction is ionisation of the carbon-halogen bond to form a carbocation.
- For comparable alkyl halides, greater carbocation stability gives a faster S_N1 reaction; tertiary carbocations are more stable than secondary ones.

Step 1: Identify the two compounds The left structure is 2-chloro-2-methylpropane, $(CH_3)_3CCl$, a tertiary chloride. The right structure is 3-chloropentane, $CH_3CH_2CHClCH_2CH_3$, a secondary chloride. Both have chloride as the leaving group, so the key difference is the carbocation formed.

Step 2: Compare the ionisation steps The left compound produces the tertiary tert-butyl carbocation, whereas the right produces a secondary carbocation. The three alkyl groups stabilise the tertiary cation through their electron-releasing inductive effect and hyperconjugation. This makes its formation easier and hence its S_N1 reaction faster.

Step 3: Conclusion 2-Chloro-2-methylpropane (the left compound) undergoes S_N1 faster because it forms the more stable tertiary carbocation.

Quick Tip to Solve: For this pair, first count alkyl groups on the carbon bearing Cl: three on the left, two on the right; S_N1 favours the tertiary centre.

21(b). Arrange the following compounds in increasing order of their reactivity towards S_N2 displacement:

2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane. [1 mark]

Solution:

Concept:

- An S_N2 reaction occurs in one step through backside attack of the nucleophile at the carbon bearing the leaving group.
- Steric hindrance reduces the rate of backside attack. With the same leaving group, the usual reactivity is primary $>$ secondary $>$ tertiary.

Step 1: Classify the carbon bonded to bromine In 2-bromo-2-methylbutane the carbon carrying Br is bonded to three carbon groups, so the compound is tertiary. In 2-bromopentane that carbon is bonded to two carbon groups, making it secondary. In 1-bromopentane the carbon bearing Br is bonded to only one carbon group, making it primary.

Step 2: Apply the steric-hindrance comparison All three compounds have Br as their leaving group. Thus, the degree of crowding near the reaction centre determines the comparison. Backside approach is most hindered at the tertiary centre and least hindered at the primary centre. Therefore, reverse the primary-to-tertiary decreasing-reactivity sequence to obtain the required increasing order.

Step 3: Conclusion The increasing order is

$$\text{2-bromo-2-methylbutane} < \text{2-bromopentane} < \text{1-bromopentane}.$$

Quick Tip to Solve: The question asks for increasing S_N2 reactivity: put the most crowded, tertiary bromide first and the primary bromide last.

Section C (21 marks)

22. At 25 °C the saturated vapour pressure of water is 24 mm Hg. Find the saturated vapour pressure of a 5% aqueous solution of urea at the same temperature. (Molar mass of urea = 60 g mol^{-1})

[3 marks]

Solution:

Concept:

- For a solution of a non-volatile solute, Raoult's law gives $p = x_{\text{water}} p^0$, where p^0 is the vapour pressure of pure water and x_{water} is its mole fraction.
- Urea is a non-volatile molecular solute and does not dissociate; its particles lower the mole fraction of water.
- A 5 percent aqueous solution by mass contains 5 g urea in 100 g solution, leaving 95 g water.

Step 1: Choose a solution sample and calculate moles Take 100 g of the aqueous solution. The mass of urea is 5 g, and the mass of water is $100 - 5 = 95$ g. Using the given urea molar mass and 18 g mol^{-1}

Quick Tip to Solve: In a 100 g sample of a 5 percent solution, use 95 g water, not 100 g water, and convert both masses to moles before using Raoult's law.

for water,

$$n_{\text{urea}} = \frac{5}{60} = \frac{1}{12}\,\text{mol}, \qquad n_{\text{water}} = \frac{95}{18}\,\text{mol}.$$

The percentage specifies the mass fraction; it must be converted to a mole fraction before applying Raoult's law.

Step 2: Calculate the water mole fraction The mole fraction is the moles of water divided by the total moles of water and urea:

$$x_{\text{water}} = \frac{95/18}{95/18 + 5/60} = \frac{570}{579} = \frac{190}{193} \approx 0.984456.$$

Correspondingly, $x_{\text{urea}} = 3/193$. These two mole fractions add to unity. Urea contributes no appreciable vapour pressure, so only the solvent mole fraction enters the vapour-pressure calculation.

Step 3: Apply Raoult's law at the given temperature At 25°C, the pure-water vapour pressure is 24 mm Hg. Therefore,

$$p = x_{\text{water}} p^0 = \frac{190}{193} \times 24 = \frac{4560}{193}\,\text{mm Hg} \approx 23.6269\,\text{mm Hg}.$$

As a check, the lowering is $24 - 23.6269 \approx 0.3731$ mm Hg, which equals $24 x_{\text{urea}}$. The pressure is slightly lower than that of pure water, as expected for a non-volatile solute.

Step 4: Conclusion The saturated vapour pressure of the solution at 25°C is $\boxed{23.63\,\text{mm Hg}}$.

Quick Tip to Solve: In a 100 g sample of a 5 percent solution, use 95 g water, not 100 g water, and convert both masses to moles before using Raoult's law.

23. The electrical resistance of a column of 0.05 M NaOH solution of area 0.8 cm^2 and length 40 cm is 5 $\times$ 10^3 ohm. Calculate its resistivity, conductivity and molar conductivity. [3 marks]

Solution:

Concept:

- Resistance depends on the dimensions of the conducting column: $R = \rho l/A$, where ρ is resistivity, l is length and A is cross-sectional area.
- Conductivity is the reciprocal of resistivity, $\kappa = 1/\rho$. When κ is in S cm^{-1} and concentration C is in mol L^{-1}, molar conductivity is $\Lambda_m = 1000\kappa/C$.

Step 1: Determine the resistivity from the cell dimensions The given values are $R = 5 \times 10^3\,\Omega$, $A = 0.8\,\text{cm}^2$, $l = 40\,\text{cm}$ and $C = 0.05\,\text{mol L}^{-1}$. Rearranging the resistance relation gives

$$\rho = \frac{RA}{l} = \frac{(5 \times 10^3)(0.8)}{40} = 100\,\Omega\,\text{cm}.$$

The cell constant is $l/A = 40/0.8 = 50\,\text{cm}^{-1}$. Using centimetres throughout keeps the calculated resistivity in $\Omega\,\text{cm}$.

Quick Tip to Solve: Keep the cell dimensions in centimetres and use the factor 1000 only when converting molarity to molar conductivity.

Step 2: Calculate conductivity and molar conductivity Taking the reciprocal of the resistivity,

$$\kappa = \frac{1}{100} = 1.0 \times 10^{-2}\,\mathrm{S\,cm^{-1}}.$$

One mole of solute occupies $1000/C$ cubic centimetres of this solution; multiplying conductivity by that volume gives

$$\Lambda_m = \frac{1000\kappa}{C} = \frac{1000(1.0 \times 10^{-2})}{0.05} = 200\,\mathrm{S\,cm^2\,mol^{-1}}.$$

As a consistency check, $\kappa = (l/A)/R = 50/5000$, reproducing the same conductivity without first calculating resistivity.

Step 3: Conclusion The resistivity is $\boxed{100\,\Omega\,\mathrm{cm}}$, conductivity is $\boxed{1.0 \times 10^{-2}\,\mathrm{S\,cm^{-1}}}$, and molar conductivity is $\boxed{200\,\mathrm{S\,cm^2\,mol^{-1}}}$.

Quick Tip to Solve: Keep the cell dimensions in centimetres and use the factor 1000 only when converting molarity to molar conductivity.

24. Complete and balance the following chemical equations:

(a) $\mathrm{MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow}$

(b) $\mathrm{KMnO_4} \xrightarrow[513\,\mathrm{K}]{\textbf{Heat}}$

(c) $\mathrm{Cr_2O_7^{2-} + H_2S + H^+ \longrightarrow}$ [3 marks]

Solution:

Concept:

- In acid, permanganate forms $\mathrm{Mn^{2+}}$ and dichromate forms $\mathrm{Cr^{3+}}$. Balance oxygen with water, hydrogen with $\mathrm{H^+}$, and charge with electrons.
- Oxalate is oxidised to carbon dioxide and hydrogen sulphide is oxidised to sulphur. Thermal decomposition of potassium permanganate forms potassium manganate, manganese dioxide and oxygen.

Step 1: (a) Balance permanganate oxidation of oxalate The reduction and oxidation half-reactions in acidic solution are

$$\mathrm{MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O},$$
$$\mathrm{C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-}.$$

Multiply the first by 2 and the second by 5 to cancel ten electrons. Thus,

$$\mathrm{2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}.$$

Both sides have total charge $+4$; the manganese, carbon, oxygen and hydrogen atoms are also balanced.

Step 2: (b) Complete the thermal decomposition At the stated temperature, $513\,\mathrm{K}$, potassium

Quick Tip to Solve: In acidic redox equations, cancel hydrogen ions after combining half-reactions and verify total charge as well as atoms.

permanganate decomposes according to

$$2\mathrm{KMnO_4} \xrightarrow[513\,\mathrm{K}]{\text{Heat}} \mathrm{K_2MnO_4} + \mathrm{MnO_2} + \mathrm{O_2}.$$

The products contain two potassium atoms, two manganese atoms and eight oxygen atoms, matching the reactants. The oxidation states of manganese change from $+7$ to $+6$ and $+4$, while oxygen gas is liberated.

Step 3: (c) Balance dichromate oxidation of hydrogen sulphide Write the corresponding half-reactions:

$$\mathrm{Cr_2O_7^{2-}} + 14\mathrm{H^+} + 6\mathrm{e^-} \longrightarrow 2\mathrm{Cr^{3+}} + 7\mathrm{H_2O},$$
$$\mathrm{H_2S} \longrightarrow \mathrm{S} + 2\mathrm{H^+} + 2\mathrm{e^-}.$$

Multiply the sulphide half-reaction by 3. On adding, cancel six electrons and six hydrogen ions to obtain

$$\mathrm{Cr_2O_7^{2-}} + 3\mathrm{H_2S} + 8\mathrm{H^+} \longrightarrow 2\mathrm{Cr^{3+}} + 3\mathrm{S} + 7\mathrm{H_2O}.$$

The total charge on each side is $+6$, and all four elements have equal atom counts on the two sides.

Step 4: Conclusion The completed, balanced equations are given in steps (a), (b) and (c). The oxidised products in the acidic reactions are respectively $\mathrm{CO_2}$ and S; heating permanganate releases $\mathrm{O_2}$.

Quick Tip to Solve: In acidic redox equations, cancel hydrogen ions after combining half-reactions and verify total charge as well as atoms.

25. Using valence bond theory, explain the hybridization and magnetic character of the following:
(a) $[Co(NH_3)_6]^{3+}$
(b) $[Ni(CO)_4]$
[At. no.: Co = 27, Ni = 28] [3 marks]

Solution:

Concept:

- In valence bond theory, the central atom supplies empty orbitals which hybridise to accept lone pairs from ligands. The coordination number fixes the number of hybrid orbitals required.
- Magnetic behaviour depends on unpaired electrons: a complex with no unpaired electrons is diamagnetic. For an octahedral complex, d^2sp^3 uses two inner $3d$ orbitals; tetrahedral sp^3 uses one $4s$ and three $4p$ orbitals.

Step 1: (a) Establish the cobalt ion configuration and pairing Each ammonia ligand is neutral, so cobalt has oxidation state $+3$ in $[\mathrm{Co(NH_3)_6}]^{3+}$. For atomic number 27,

$$\mathrm{Co} : [\mathrm{Ar}]\,3d^7 4s^2, \qquad \mathrm{Co^{3+}} : [\mathrm{Ar}]\,3d^6.$$

Electrons are removed from $4s$ before $3d$. In this cobalt(III) complex, the ammonia ligands cause pairing of the six $3d$ electrons. Three $3d$ orbitals become doubly occupied and the other two become

Quick Tip to Solve: Find the metal oxidation state before counting d electrons; neutral CO leaves nickel at zero, unlike ammonia around cobalt(III).

empty.

Step 2: Identify the cobalt hybridisation and magnetism The two empty inner $3d$ orbitals, one empty $4s$ orbital and three empty $4p$ orbitals hybridise to form six d^2sp^3 orbitals. These accept one lone pair from each of the six ammonia ligands, giving an octahedral, inner-orbital complex. All six $3d$ electrons are paired, so the number of unpaired electrons is zero and the complex is diamagnetic.

Step 3: (b) Establish the nickel configuration and hybridisation Carbon monoxide is a neutral ligand; hence the nickel oxidation state in $[\mathrm{Ni(CO)_4}]$ is zero. With atomic number 28, free nickel has configuration $[\mathrm{Ar}]\,3d^8 4s^2$. Under the influence of strong-field CO ligands, the two $4s$ electrons enter the $3d$ subshell, producing a fully paired $3d^{10}$ arrangement and leaving $4s$ empty. The empty $4s$ orbital and three empty $4p$ orbitals undergo sp^3 hybridisation. Their four hybrid orbitals accept lone pairs from four CO ligands and are directed tetrahedrally. Since the filled $3d$ subshell contains no unpaired electron, the complex is diamagnetic.

Step 4: Conclusion $[\mathrm{Co(NH_3)_6}]^{3+}$ has $\boxed{d^2sp^3}$ hybridisation, octahedral geometry and diamagnetic character. $[\mathrm{Ni(CO)_4}]$ has $\boxed{sp^3}$ hybridisation, tetrahedral geometry and is also diamagnetic.

Quick Tip to Solve: Find the metal oxidation state before counting d electrons; neutral CO leaves nickel at zero, unlike ammonia around cobalt(III).

26(a). Define the following:

(i) Enantiomers

(ii) Racemic mixture [2 marks]

Solution:

Concept:

- Stereoisomers have the same connectivity of atoms but differ in their arrangement in space. Chirality is the property of not being superimposable on the mirror image.
- Optical activity means rotation of plane-polarised light. The two members of an enantiomeric pair rotate light equally in opposite directions under identical conditions.

Step 1: Define enantiomers Enantiomers are stereoisomers that are non-superimposable mirror images of one another. Their atoms are connected in the same order, but their three-dimensional arrangements differ. For example, the two mirror-image configurations of butan-2-ol form an enantiomeric pair. One enantiomer is dextrorotatory and the other is laevorotatory; the magnitude of rotation is equal when concentration, path length and measurement conditions are identical.

Step 2: Define a racemic mixture A racemic mixture is an equimolar mixture of the two enantiomers of an optically active compound. It contains equal amounts of the dextrorotatory and laevorotatory forms. Their equal and opposite rotations cancel, so the mixture shows zero net optical rotation. This

Quick Tip to Solve: Include both mirror-image non-superimposability in the first definition and equal amounts with cancellation of rotation in the second.

optical inactivity results from external compensation between separate molecules, rather than from the absence of chirality in each molecule.

Step 3: Conclusion Enantiomers are non-superimposable mirror-image stereoisomers; a racemic mixture contains equal amounts of the two enantiomers and is optically inactive by external compensation.

Quick Tip to Solve: Include both mirror-image non-superimposability in the first definition and equal amounts with cancellation of rotation in the second.

26(b). Why is chlorobenzene resistant to nucleophilic substitution reaction? [1 mark]

Solution:

Concept:

- Resonance is delocalisation of electrons over adjacent orbitals. A bond with partial double-bond character is shorter and stronger than an ordinary single bond.
- Nucleophilic substitution requires cleavage of the carbon-halogen bond. The geometry and stability of possible intermediates affect the ease of this cleavage.

Step 1: Examine the carbon-chlorine bond In chlorobenzene, a lone pair on chlorine is delocalised into the benzene ring by resonance. Consequently, the $\mathrm{C-Cl}$ bond acquires partial double-bond character. Also, chlorine is bonded to an sp^2-hybridised carbon. The bond is therefore shorter and stronger than the carbon-chlorine bond in an alkyl chloride, so it is difficult to cleave.

Step 2: Relate the structure to substitution The usual S_N1 pathway is disfavoured because breaking the bond would form a highly unstable phenyl carbocation. The usual S_N2 pathway is also difficult at the aryl carbon because effective backside attack is hindered by the aromatic ring framework and electron cloud. Thus ordinary alkyl-halide substitution conditions are ineffective.

Step 3: Conclusion Chlorobenzene resists nucleophilic substitution mainly because resonance gives its short, strong $\mathrm{C-Cl}$ bond partial double-bond character.

Quick Tip to Solve: Connect chlorine lone-pair resonance directly to partial double-bond character, increased bond strength and difficult bond cleavage.

27(A)(a). Explain the following reactions and write chemical equation involved:

Wolff-Kishner reduction [1 mark]

Solution:

Concept:

- Wolff-Kishner reduction converts an aldehyde or ketone carbonyl group into a methylene group using hydrazine and strong base on heating.
- The carbonyl compound first forms a hydrazone, which then loses nitrogen during reduction; the carbon skeleton is retained.

Quick Tip to Solve: Remember hydrazine plus hot KOH for Wolff-Kishner reduction, and replace only the carbonyl oxygen with two hydrogens.

Step 1: State the reaction and conditions An aldehyde or ketone is treated with hydrazine, NH_2NH_2, followed by heating with KOH in a high-boiling solvent such as ethylene glycol. The oxygen of the carbonyl group is ultimately replaced by two hydrogen atoms. The strongly basic conditions distinguish this method from Clemmensen reduction, which uses an acidic medium.

Step 2: Write a balanced example For acetone, hydrazone formation is followed by reduction to propane:

$$CH_3COCH_3 + H_2NNH_2 \xrightarrow{\text{KOH, heat}} CH_3CH_2CH_3 + N_2 + H_2O.$$

Nitrogen gas and water account for the nitrogen and oxygen removed from the reactants. No carbon-carbon bond is lost in this conversion.

Step 3: Conclusion Wolff-Kishner reduction changes $C = O$ to CH_2 using hydrazine and hot alkali; acetone gives propane.

Quick Tip to Solve: Remember hydrazine plus hot KOH for Wolff-Kishner reduction, and replace only the carbonyl oxygen with two hydrogens.

27(A)(b). Explain the following reactions and write chemical equation involved:

Etard reaction [1 mark]

Solution:

Concept:

- The Etard reaction selectively oxidises a methyl group attached to an aromatic ring to an aldehyde group using chromyl chloride.
- Chromyl chloride, CrO_2Cl_2, forms an intermediate complex in a non-aqueous solvent; hydrolysis liberates the aromatic aldehyde.

Step 1: Explain the conversion Toluene is treated with chromyl chloride in carbon disulphide or carbon tetrachloride. The methyl side chain forms the Etard complex. Hydrolysis of this complex gives benzaldehyde, while the aromatic ring remains intact. This controlled oxidation stops at the aldehyde, unlike vigorous oxidation with hot permanganate, which produces benzoic acid.

Step 2: Write the reaction equation The standard reaction scheme is

$$C_6H_5CH_3 \xrightarrow[CS_2]{CrO_2Cl_2} \text{Etard complex} \xrightarrow{H_2O} C_6H_5CHO.$$

Equivalently, the organic oxidation balance is

$$C_6H_5CH_3 + 2[O] \longrightarrow C_6H_5CHO + H_2O.$$

The product has one aldehydic hydrogen on the side-chain carbon.

Step 3: Conclusion Etard oxidation converts toluene into benzaldehyde by chromyl chloride treatment followed by hydrolysis.

Quick Tip to Solve: For Etard reaction, pair chromyl chloride with toluene and stop at benzaldehyde rather than writing benzoic acid.

27(A)(c). Explain the following reactions and write chemical equation involved:

Cannizzaro reaction [1 mark]

Solution:

Concept:

- Aldehydes without an alpha hydrogen undergo Cannizzaro disproportionation in concentrated aqueous alkali.
- Disproportionation means simultaneous oxidation and reduction of the same reactant: one aldehyde molecule gives a carboxylate and another gives an alcohol.

Step 1: State the condition and products An aldehyde that lacks hydrogen on the carbon adjacent to its carbonyl group reacts with concentrated sodium hydroxide or potassium hydroxide. Two molecules participate: one is oxidised to the salt of the corresponding carboxylic acid and the other is reduced to the corresponding primary alcohol. Benzaldehyde qualifies because it has no alpha hydrogen.

Step 2: Write a balanced equation Using benzaldehyde as the example,

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH.$$

The products are sodium benzoate and benzyl alcohol. The acid appears as its sodium salt because the reaction occurs in a strongly alkaline medium. Writing two aldehyde molecules is essential to represent the oxidation and reduction together.

Step 3: Conclusion Cannizzaro reaction is disproportionation of an aldehyde without alpha hydrogen in concentrated alkali, producing a carboxylate salt and a primary alcohol.

Quick Tip to Solve: Check for absence of alpha hydrogen, then write two aldehyde molecules and one molecule each of carboxylate salt and alcohol.

OR

27(B)(a). Write the structures of A, B and C in the following sequence of reactions: [1.5 marks]

$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow{H_2,\ Pd\text{-}BaSO_4} B \xrightarrow{H_2N\text{–}NH_2} C$$

Solution:

Concept:

- Thionyl chloride converts a carboxylic acid into its acyl chloride by replacing the hydroxyl group with chlorine.
- Rosenmund reduction uses hydrogen and palladium on barium sulphate to reduce an acyl chloride selectively to an aldehyde.
- An aldehyde reacts with hydrazine by condensation to give a hydrazone, replacing carbonyl oxygen with $= NNH_2$.

Step 1: Identify the product of thionyl chloride Ethanoic acid reacts with thionyl chloride to form

Quick Tip to Solve: Recognise acid chloride formation, then Rosenmund reduction; hydrazine without hot alkali stops at the hydrazone.

ethanoyl chloride. The methyl group and carbonyl carbon remain unchanged:

$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl.$$

Thus the first intermediate is an acyl chloride, not chloroethane; the carbonyl oxygen remains present in the molecule.

Step 2: Apply Rosenmund reduction Hydrogen in the presence of palladium supported on barium sulphate reduces the acyl chloride to ethanal:

$$CH_3COCl + H_2 \xrightarrow{Pd-BaSO_4} CH_3CHO + HCl.$$

The moderated catalyst allows the reduction to stop at the aldehyde rather than continuing to the primary alcohol.

Step 3: Condense ethanal with hydrazine Ethanal combines with hydrazine and eliminates water to form its hydrazone:

$$CH_3CHO + H_2N - NH_2 \longrightarrow CH_3CH = NNH_2 + H_2O.$$

The nitrogen initially bearing two hydrogens forms the carbon-nitrogen double bond. Hydrazine alone gives the hydrazone; conversion to ethane by Wolff-Kishner reduction would additionally require strong alkali and heating, which are absent from the printed sequence.

Step 4: Conclusion The required structures are $\boxed{A = CH_3C(=O)Cl}$, $\boxed{B = CH_3C(=O)H}$ and $\boxed{C = CH_3CH = NNH_2}$.

Quick Tip to Solve: Recognise acid chloride formation, then Rosenmund reduction; hydrazine without hot alkali stops at the hydrazone.

27(B)(b). Write the structures of A, B and C in the following sequence of reactions:

$$CH_3CN \xrightarrow[2.\ H_2O]{1.\ DIBAL-H} A \xrightarrow{Dil\cdot\ NaOH} B \xrightarrow{\Delta} C$$

[1.5 marks]

Solution:

Concept:

- DIBAL-H partially reduces a nitrile to an imine intermediate; hydrolysis then gives an aldehyde with the same number of carbon atoms.
- An aldehyde containing an alpha hydrogen undergoes aldol addition with dilute $NaOH$. Heating the beta-hydroxy aldehyde eliminates water to form an alpha,beta-unsaturated aldehyde.

Step 1: Identify A after partial reduction The nitrile CH_3CN has two carbon atoms. DIBAL-H followed by hydrolysis changes its nitrile group into an aldehyde group without removing a carbon atom. Therefore A is ethanal, CH_3CHO. This is controlled partial reduction; the product is not ethanol or

Quick Tip to Solve: Count carbons at each stage: nitrile reduction preserves two carbons, aldol addition doubles them to four, and heating removes only water.

ethylamine.

Step 2: Identify B by aldol addition Ethanal has alpha hydrogens. In dilute NaOH, two molecules of ethanal combine: one supplies the enolate nucleophile and the other supplies the carbonyl group. The product is the beta-hydroxy aldehyde 3-hydroxybutanal:

$$2\,\mathrm{CH_3CHO} \xrightarrow{\text{dil. NaOH}} \mathrm{CH_3CH(OH)CH_2CHO}.$$

Thus B has four carbon atoms and retains an aldehyde group.

Step 3: Identify C after heating Heating B removes its beta hydroxyl group together with an alpha hydrogen as water, forming the conjugated double bond:

$$\mathrm{CH_3CH(OH)CH_2CHO} \xrightarrow{\Delta} \mathrm{CH_3CH{=}CHCHO} + \mathrm{H_2O}.$$

C is but-2-enal (crotonaldehyde). The four-carbon chain remains intact in this dehydration.

Step 4: Conclusion A: $\boxed{\mathrm{CH_3CHO}}$; B: $\boxed{\mathrm{CH_3CH(OH)CH_2CHO}}$; C: $\boxed{\mathrm{CH_3CH{=}CHCHO}}$.

Quick Tip to Solve: Count carbons at each stage: nitrile reduction preserves two carbons, aldol addition doubles them to four, and heating removes only water.

28. Define the following terms:

(a) Glycosidic linkage

(b) Invert sugar

(c) Oligosaccharides [3 marks]

Solution:

Concept:

- Carbohydrates can be classified by the number of monosaccharide units obtained on hydrolysis; their units are joined through glycosidic linkages.
- Optical rotation distinguishes dextrorotatory and laevorotatory substances. Hydrolysis of sucrose changes the sign of the observed rotation.

Step 1: Define glycosidic linkage A glycosidic linkage is the oxygen-containing linkage joining two monosaccharide units, formed by loss of a water molecule between their hydroxyl groups. It is a $\mathrm{C{-}O{-}C}$ bridge involving an anomeric carbon of a sugar. For example, in maltose, the linkage joins carbon 1 of one glucose unit to carbon 4 of the second glucose unit. Hydrolysis cleaves the linkage and restores the constituent monosaccharides.

Step 2: Define invert sugar Invert sugar is the equimolar mixture of glucose and fructose obtained by hydrolysis of sucrose:

$$\mathrm{C_{12}H_{22}O_{11}} + \mathrm{H_2O} \longrightarrow \mathrm{C_6H_{12}O_6} + \mathrm{C_6H_{12}O_6}.$$

The products are glucose and fructose, respectively. Sucrose is dextrorotatory, whereas the hydrolysis mixture is laevorotatory because the negative rotation of fructose exceeds the positive rotation of glucose. This change in the sign of rotation is called inversion, giving the mixture its name.

Quick Tip to Solve: For invert sugar, mention both the glucose-fructose mixture and the reversal from positive to negative optical rotation; for oligosaccharides, give the range two to ten.

Step 3: Define oligosaccharides Oligosaccharides are carbohydrates which, on hydrolysis, yield two to ten monosaccharide units. They are further classified as disaccharides, trisaccharides and so on, according to that number. Sucrose and maltose are disaccharides and therefore oligosaccharides; carbohydrates yielding many more units belong to the polysaccharide category.

Step 4: Conclusion Glycosidic linkage joins monosaccharide units through oxygen; invert sugar is the equimolar glucose-fructose mixture from sucrose hydrolysis; oligosaccharides yield two to ten monosaccharide units on hydrolysis.

Quick Tip to Solve: For invert sugar, mention both the glucose-fructose mixture and the reversal from positive to negative optical rotation; for oligosaccharides, give the range two to ten.

Section D (8 marks)

29(a). Read the passage and answer: The spontaneous flow of the solvent through a semipermeable membrane from a pure solvent to a solution or from a dilute solution to a concentrated solution is called osmosis. The phenomenon of osmosis can be demonstrated by taking two eggs of the same size. In an egg, the membrane below the shell and around the egg material is semipermeable. The outer hard shell can be removed by putting the egg in dilute hydrochloric acid. After removing the hard shell, one egg is placed in distilled water and the other in a saturated salt solution. After some time, the egg placed in distilled water swells-up while the egg placed in salt solution shrinks. The external pressure applied to stop the osmosis is termed as osmotic pressure (a colligative property). Reverse osmosis takes place when the applied external pressure becomes larger than the osmotic pressure.

(a) Define reverse osmosis. Name one SPM which can be used in the process of reverse osmosis.

[2 marks]

Solution:

Concept:

- Osmosis is the flow of solvent through a semipermeable membrane from the pure solvent or dilute side to the more concentrated solution.
- Osmotic pressure π is the external pressure needed to stop osmosis. Reversing the flow requires an applied pressure greater than π on the solution side.

Step 1: Define reverse osmosis and its condition Reverse osmosis is the flow of solvent from the solution side to the pure-solvent side through a semipermeable membrane when a pressure greater than the osmotic pressure is applied to the solution. Thus, for a solution against pure solvent, the required condition is $P_{\text{applied}} > \pi$. Merely applying a pressure equal to π stops the net flow; it does not reverse it.

Step 2: Name a suitable semipermeable membrane A cellulose acetate membrane is suitable for reverse osmosis. It allows water molecules to pass while retaining dissolved salts and other solutes. The membrane is supported so that it can withstand the large applied pressure. Consequently, pressurised saline water yields water with a reduced salt content on the other side, which explains the use of this process in desalination.

Quick Tip to Solve: Always place the applied pressure on the solution side: equality with osmotic pressure stops flow, whereas greater pressure reverses it.

Step 3: Conclusion Reverse osmosis drives solvent from solution to pure solvent through an SPM under $P_{\text{applied}} > \pi$. One suitable SPM is a cellulose acetate membrane.

Quick Tip to Solve: Always place the applied pressure on the solution side: equality with osmotic pressure stops flow, whereas greater pressure reverses it.

29(b). What do you expect to happen when red blood corpuscles (RBC's) are placed in 0.5% NaCl solution? [1 mark]

Solution:

Concept:

- A solution isotonic with red blood corpuscles contains approximately 0.9% NaCl; a lower salt concentration is hypotonic.
- Across the semipermeable cell membrane, water moves by osmosis towards the side with the greater effective solute concentration.

Step 1: Compare the salt concentration The given 0.5% NaCl solution is more dilute than the approximately 0.9% saline solution isotonic with RBCs. Its osmotic pressure is therefore lower than that of the fluid inside the cells. The external medium is hypotonic, rather than hypertonic.

Step 2: Determine the movement of water and the cell response Water enters the RBCs through their semipermeable membranes by osmosis (endosmosis). The cells increase in volume and swell. Since RBCs lack a rigid cell wall, continued entry of water can rupture their membranes, producing haemolysis. Shrinkage would instead occur in a hypertonic saline solution.

Step 3: Conclusion RBCs placed in 0.5% NaCl swell due to endosmosis and may burst (haemolysis).

Quick Tip to Solve: Compare the salt percentage with isotonic saline, about 0.9%: below it RBCs swell, while above it they shrink.

OR

29(b). Which one of the following will have higher osmotic pressure in 1M KCl or 1M urea solution. Justify your answer. [1 mark]

Solution:

Concept:

- For a dilute solution, osmotic pressure is $\pi = iCRT$, where i is the van't Hoff factor, C is molarity, R is the gas constant and T is absolute temperature.
- Osmotic pressure depends on the total number of dissolved particles, including ions formed by dissociation.

Step 1: Compare the particle numbers KCl is an electrolyte and dissociates as $\text{KCl} \longrightarrow \text{K}^+ + \text{Cl}^-$. Each formula unit supplies two ions in the ideal complete-dissociation limit, so $i \approx 2$. Urea, $\text{CO}(\text{NH}_2)_2$, is a non-electrolyte and remains as molecules in solution, giving $i = 1$.

Quick Tip to Solve: For equal molarity and temperature, compare van't Hoff factors: count two ions for KCl but one undissociated molecule for urea.

Step 2: Apply the osmotic-pressure relation At the same temperature, both solutions have the same molarity, $C = 1\,\text{mol}\,\text{L}^{-1}$. Hence $\pi_{\text{KCl}} \approx 2CRT$ and $\pi_{\text{urea}} = CRT$. Dissociation therefore makes the particle concentration, and consequently the osmotic pressure, greater for potassium chloride. Equal molarity alone does not imply equal osmotic pressure for an electrolyte and a non-electrolyte.

Step 3: Conclusion The $1\,\text{M}$ KCl solution has the higher osmotic pressure because it dissociates into two ions, whereas urea does not dissociate.

Quick Tip to Solve: For equal molarity and temperature, compare van't Hoff factors: count two ions for KCl but one undissociated molecule for urea.

29(c). Why osmotic pressure is a colligative property? [1 mark]

Solution:

Concept:

- A colligative property depends on the number of dissolved solute particles, rather than their chemical identity.
- For a dilute solution, $\pi = CRT = nRT/V$, where π is osmotic pressure, C is particle concentration, R is the gas constant and T is absolute temperature.

Step 1: Apply the osmotic-pressure relation At a fixed temperature and solution volume, $\pi = nRT/V$ depends only on the number of moles of solute particles. No term in this expression specifies the chemical nature of the solute.

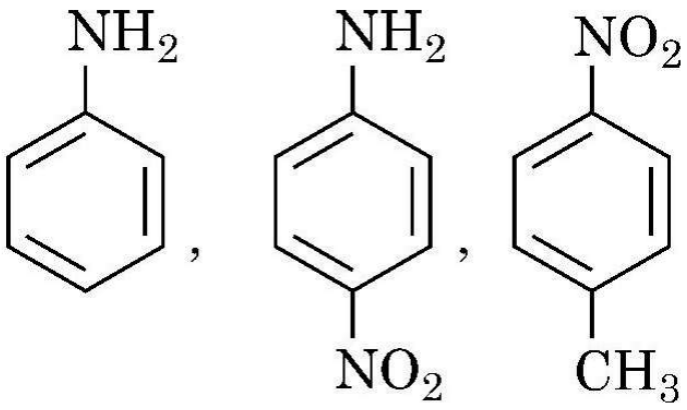
Step 2: Compare equal particle concentrations Two dilute solutions containing the same concentration of dissolved particles have the same osmotic pressure at the same temperature. For electrolytes, count the ions produced by dissociation; the expression is $\pi = iCRT$, with i the vanŕ Hoff factor.

Step 3: Conclusion Osmotic pressure is a colligative property because it depends on the number of solute particles per unit volume, not their chemical nature, at a fixed temperature.

Quick Tip to Solve: For osmotic pressure, compare particle concentrations at the same temperature; count dissociated ions separately.

30(a). **Read the passage and answer: Amines have a lone pair of electrons on nitrogen atom due to which they behave as Lewis base. Greater the value of K_b or smaller the value of pK_b, stronger is the base. Amines are more basic than alcohols, ethers, esters, etc. The basic character of aliphatic amines should increase with the increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in aqueous solutions. Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron releasing groups such as -CH_3, -OCH_3, -NH_2, etc., increase the basicity while electron-withdrawing substituents such as -NO_2, -CN, halogens etc., decrease the basicity of amines. The effect of these substitute is more at p- than at m- position.**

(a) Arrange the following in the increasing order of their basic character. Give reason: [2 marks]



Solution:

Concept:

- Basicity depends on availability of an electron pair for proton acceptance; greater K_b means a stronger base.
- An amino group provides a nitrogen lone pair. A para nitro group withdraws electron density by inductive and resonance effects.

Step 1: Identify all three printed structures The structures are aniline, p-nitroaniline and p-nitrotoluene. The third has $-NO_2$ and $-CH_3$, with no amino group: its nitro nitrogen has no available lone pair, and proton acceptance at nitro oxygen is very weak.

Step 2: Compare their proton-accepting ability Aniline accepts a proton using its amino nitrogen lone pair. In p-nitroaniline, the $-NO_2$ group withdraws electron density and decreases the availability of that pair, lowering basicity. Nevertheless, its amino group makes it more basic than p-nitrotoluene. The methyl group in the latter does not compensate for the absence of an amino group.

Step 3: Conclusion The increasing order is

$$p\text{-nitrotoluene} < p\text{-nitroaniline} < \text{aniline}.$$

Quick Tip to Solve: Inspect the actual groups first: the third printed ring has nitro and methyl groups, with no amino group.

30(b). Why pK_b of aniline is more than that of methylamine? [1 mark]

Solution:

Concept:

- $pK_b = -\log_{10} K_b$; a larger pK_b means a weaker base.
- A base accepts a proton using its available lone pair; resonance delocalisation reduces the availability of the nitrogen lone pair.

Step 1: Examine the lone pair in aniline In aniline, the nitrogen lone pair is conjugated with the benzene ring and becomes delocalised by resonance. It is therefore less available to accept a proton, making aniline a relatively weak base.

Step 2: Compare methylamine In methylamine, the nitrogen lone pair is localised. The methyl group also exerts a positive inductive effect, increasing electron density on nitrogen. Hence methylamine accepts a proton more readily and has a larger K_b than aniline. Taking the negative logarithm reverses this comparison.

Step 3: Conclusion Aniline has a larger pK_b because it is less basic than methylamine: its lone pair is delocalised into the ring, whereas methylamine has a localised lone pair enhanced by the $+I$ effect of $-CH_3$.

Quick Tip to Solve: First compare lone-pair availability, then reverse the basicity order when comparing values of pK_b.

30(c). Arrange the following in the increasing order of their basic character in an aqueous solution:
$(CH_3)_3N,\ (CH_3)_2NH,\ NH_3,\ CH_3NH_2$ [1 mark]

Solution:

Concept:

- In aqueous solution, alkylamine basicity depends on the electron-releasing inductive effect and hydration of the conjugate acid.
- For methylamines in water, the secondary amine is strongest; reduced hydration lowers the basicity of the tertiary amine.

Step 1: Compare ammonia with methylamines Methyl groups release electron density towards nitrogen through the $+I$ effect. Consequently, all three methylamines are more basic than ammonia, whose nitrogen has no electron-releasing methyl substituent.

Step 2: Include hydration in water The protonated secondary amine combines strong electron donation with effective hydration and is the most stable conjugate acid in this series. Protonated trimethylamine is less effectively hydrated because of its three methyl groups and fewer N–H bonds.

Quick Tip to Solve: For methylamines in water, remember secondary > primary > tertiary > ammonia; hydration changes the simple inductive order.

For the methylamine series, this hydration disadvantage makes trimethylamine weaker than methylamine, despite its greater inductive donation.

Step 3: Conclusion The increasing order in aqueous solution is

$$NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH.$$

Quick Tip to Solve: For methylamines in water, remember secondary > primary > tertiary > ammonia; hydration changes the simple inductive order.

OR

30(c). Why ammonolysis of alkyl halides is not a good method to prepare pure amines? [1 mark]

Solution:

Concept:

- Ammonolysis replaces the halogen in an alkyl halide by an amino group using ammonia.
- The primary amine produced still has a nitrogen lone pair and can react further with alkyl halide.

Step 1: Consider the first substitution An alkyl halide reacts with ammonia to give a primary amine after removal of a proton. For example,

$$RCl + 2NH_3 \longrightarrow RNH_2 + NH_4Cl.$$

The reaction does not automatically stop after this substitution.

Step 2: Follow further alkylation The primary amine also attacks alkyl halide, producing a secondary amine; further alkylation gives a tertiary amine and then a quaternary ammonium salt. The resulting mixture is difficult to separate into pure individual amines. Excess ammonia favours the primary amine but does not make the process intrinsically selective.

Step 3: Conclusion Ammonolysis is unsuitable for preparing pure amines because successive alkylation produces a mixture of primary, secondary and tertiary amines and quaternary ammonium salts.

Quick Tip to Solve: Trace the sequence primary amine to secondary to tertiary to quaternary salt whenever ammonolysis purity is asked.

Section E (15 marks)

31(A)(a). Give IUPAC name of CH_3-CH=CH-CHO. [1 mark]

Solution:

Concept:

- The aldehyde group $-CHO$ is the principal functional group and contributes carbon 1 to the parent chain.

Quick Tip to Solve: Include the aldehyde carbon in the chain and always number it 1 before locating the C=C bond.

- An alkene aldehyde uses the suffix $-\text{enal}$, with the double-bond locant counted from the aldehyde carbon.

Step 1: Choose and number the parent chain The chain in $CH_3 - CH = CH - CHO$ contains four carbon atoms, including the aldehyde carbon. Numbering from $-CHO$ gives carbon 1 to that group and the terminal methyl carbon number 4, so the parent stem is but-.

Step 2: Locate the double bond and apply the suffix The carbon–carbon double bond lies between carbons 2 and 3, so its locant is 2. Combining the four-carbon stem, the double-bond locant and the aldehyde suffix gives but-2-enal. The printed condensed formula supplies no stereochemical information, so an E or Z descriptor cannot be assigned.

Step 3: Conclusion The IUPAC name is $\boxed{\text{but-2-enal}}$.

Quick Tip to Solve: Include the aldehyde carbon in the chain and always number it 1 before locating the C=C bond.

31(A)(b). Give a simple chemical test to distinguish between propanal and propanone. [1 mark]

Solution:

Concept:

- Tollens' reagent is ammoniacal silver nitrate containing $[Ag(NH_3)_2]^+$. An aldehyde reduces it to metallic silver while being oxidised to a carboxylate ion.
- Propanal, CH_3CH_2CHO, has an aldehyde group; propanone, CH_3COCH_3, is a simple ketone and does not give this test.

Step 1: Add Tollens' reagent Take the two samples in separate clean test tubes, add freshly prepared Tollens' reagent and warm gently in a water bath. Propanal deposits a silver mirror on the tube wall. Its oxidation is represented by

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + 2Ag + 4NH_3 + 2H_2O.$$

Step 2: Compare the observations Propanone gives no silver mirror under the same conditions because it does not reduce Tollens' reagent. A test such as 2,4-DNP would give a precipitate with both carbonyl compounds and therefore would not distinguish them.

Step 3: Conclusion Propanal gives a silver mirror with Tollens' reagent; propanone does not.

Quick Tip to Solve: Use Tollens' reagent to distinguish an aldehyde from a simple ketone; compare the silver-mirror observations.

31(A)(c). How will you convert the following:

(i) Toluene to benzoic acid

(ii) Ethanol to propan-2-ol

(iii) Propanal to 2-hydroxy propanoic acid [3 marks]

Solution:

Concept:

- Hot alkaline potassium permanganate oxidises an alkyl side chain attached to benzene to a carboxylate group. Acidification gives the free carboxylic acid.
- A Grignard reagent adds its alkyl group to a carbonyl carbon. Addition of methylmagnesium bromide to ethanal, followed by hydrolysis, gives a secondary alcohol with three carbon atoms.
- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid with halogen; aqueous alkali then replaces the halogen with hydroxyl.

Step 1: (i) Oxidise toluene to benzoic acid Heat toluene with alkaline $KMnO_4$. The methyl side chain is oxidised to potassium benzoate. Acidify the product with dilute acid to obtain benzoic acid:

$$C_6H_5CH_3 \xrightarrow[\Delta]{KMnO_4/OH^-} C_6H_5COO^-K^+ \xrightarrow{H^+} C_6H_5COOH.$$

The benzene ring is retained while its side chain becomes the carboxyl group.

Step 2: (ii) Convert ethanol to propan-2-ol Pass ethanol vapour over heated copper at $573\,K$ to form ethanal by dehydrogenation. Treat the ethanal with methylmagnesium bromide in dry ether, then hydrolyse with dilute acid:

$$CH_3CH_2OH \xrightarrow[573\,K]{Cu} CH_3CHO + H_2,$$
$$CH_3CHO + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3CH(OMgBr)CH_3,$$
$$CH_3CH(OMgBr)CH_3 \xrightarrow{H_3O^+} CH_3CH(OH)CH_3.$$

The methyl group supplied by the Grignard reagent adds the extra carbon. Water must be excluded during addition because it destroys the Grignard reagent.

Step 3: (iii) Convert propanal to 2-hydroxypropanoic acid First oxidise propanal to propanoic acid with acidified potassium dichromate. Carry out alpha bromination using Br_2 and red phosphorus, followed by water, to obtain 2-bromopropanoic acid. Heat this with aqueous alkali and acidify:

$$CH_3CH_2CHO \xrightarrow{K_2Cr_2O_7/H^+} CH_3CH_2COOH,$$
$$CH_3CH_2COOH \xrightarrow[\text{then } H_2O]{Br_2/\text{red P}} CH_3CHBrCOOH,$$
$$CH_3CHBrCOOH \xrightarrow[\text{then } H^+]{\text{aq. NaOH, }\Delta} CH_3CH(OH)COOH.$$

This route keeps all three carbon atoms and introduces hydroxyl specifically at carbon 2. Direct cyanohydrin formation from propanal would add a carbon and therefore would not give the requested three-carbon acid.

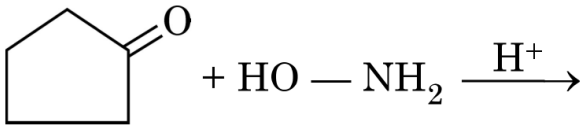
Quick Tip to Solve: Count carbons first: use a methyl Grignard reagent to add one carbon, but use HVZ when the acid skeleton must remain unchanged.

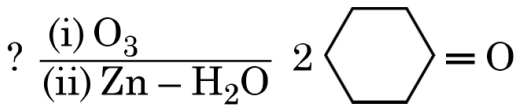
Step 4: Conclusion The required routes are side-chain oxidation and acidification for (i), ethanal formation followed by methyl Grignard addition for (ii), and oxidation, alpha bromination and hydrolysis for (iii).

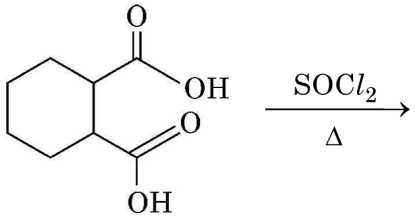
Quick Tip to Solve: Count carbons first: use a methyl Grignard reagent to add one carbon, but use HVZ when the acid skeleton must remain unchanged.

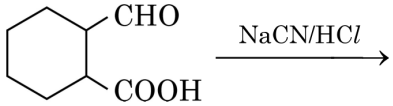
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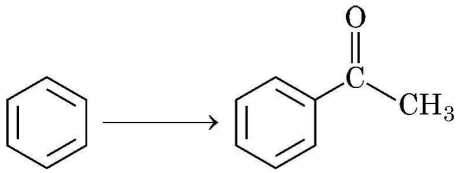
31(B). Complete each synthesis by giving missing starting material, reagent or products: [5 marks]

(a) 

(b) 

(c) 

(d) 

(e) 

Solution:

Concept:

- Hydroxylamine, NH_2OH, condenses with a ketone to give its oxime: the carbonyl group becomes $C{=}N{-}OH$, with loss of water.
- Reductive ozonolysis cleaves an alkene double bond into carbonyl groups. To reconstruct the alkene, join the two carbonyl carbons with a double bond and remove their oxygen atoms.
- Thionyl chloride, $SOCl_2$, converts carboxylic acid groups $-COOH$ into acyl chloride groups $-COCl$,

Quick Tip to Solve: Reconstruct an alkene by joining the two ozonolysis carbonyl carbons; with thionyl chloride, replace each acid OH by Cl and retain the carbonyl oxygen and ring skeleton.

releasing SO_2 and HCl.

- $NaCN/HCl$ supplies HCN for cyanohydrin formation. Friedel-Crafts acylation uses an acyl chloride with anhydrous $AlCl_3$ to introduce an acyl group into benzene.

Step 1: (a) Form cyclopentanone oxime The five-membered cyclic ketone reacts with hydroxylamine in acid to form cyclopentanone oxime. The carbonyl carbon remains part of the ring and becomes doubly bonded to nitrogen:

$$(CH_2)_4C{=}O + NH_2OH \xrightarrow{H^+} (CH_2)_4C{=}N{-}OH + H_2O.$$

In these condensed cyclic formulae, the four methylene groups form a chain whose two ends attach to the indicated carbon. Thus the ring is retained; only the carbonyl oxygen is replaced by the oxime group.

Step 2: (b) Reconstruct the starting alkene The printed product is two molecules of cyclohexanone. Each alkene carbon must therefore belong to a separate six-membered ring. The missing alkene is cyclohexylidenecyclohexane, in which a double bond joins one carbon of each ring:

$$(CH_2)_5C{=}C(CH_2)_5 \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} 2\,(CH_2)_5C{=}O.$$

Each methylene chain closes onto its own double-bonded carbon. Ozonolysis cleaves the bond joining the rings and converts both carbons into ketone groups. A double bond inside one ring would instead open that ring and could not produce two intact cyclohexanone rings.

Step 3: (c) Convert both acid groups to acyl chlorides The starting material is cyclohexane-1,2-dicarboxylic acid: the ring bears two adjacent $-COOH$ groups. On heating with thionyl chloride, each acid hydroxyl is replaced by chlorine while both carbonyl oxygen atoms remain:

$$C_6H_{10}(COOH)_2 + 2\,SOCl_2 \xrightarrow{\Delta} C_6H_{10}(COCl)_2 + 2\,SO_2 + 2\,HCl.$$

The missing product is the corresponding bis(acid chloride), cyclohexane-1,2-dicarbonyl dichloride. It has the same cyclohexane ring bearing adjacent $-C(=O)Cl$ groups. The two substitutions occur at the acid groups; the saturated ring skeleton and the positions of its substituents do not change.

Step 4: (d) Form the aldehyde cyanohydrin The reagent mixture generates HCN. Cyanide adds to the aldehyde carbonyl carbon, and protonation gives the cyanohydrin:

$$-CHO + HCN \longrightarrow -CH(OH)CN.$$

The missing product is the cyclohexane ring with adjacent $-CH(OH)CN$ and $-COOH$ substituents. The original aldehyde oxygen becomes the hydroxyl oxygen, and cyanide supplies the new nitrile carbon. The carboxylic acid group remains unchanged under the cyanohydrin-forming conditions. Thus only the aldehyde substituent is transformed.

Step 5: (e) Acylate benzene to give acetophenone Use ethanoyl chloride (acetyl chloride), CH_3COCl, and anhydrous aluminium chloride. Friedel-Crafts acylation introduces the acetyl group onto benzene:

$$C_6H_6 + CH_3COCl \xrightarrow{\text{anhydrous } AlCl_3} C_6H_5COCH_3 + HCl.$$

Quick Tip to Solve: Reconstruct an alkene by joining the two ozonolysis carbonyl carbons; with thionyl chloride, replace each acid OH by Cl and retain the carbonyl oxygen and ring skeleton.

Aluminium chloride helps generate the electrophilic acyl species from the acyl chloride. Substitution of a ring hydrogen by the acetyl group produces acetophenone, matching the printed ketone. The carbonyl group comes from the acylating reagent.

Step 6: Conclusion (a) Cyclopentanone oxime; (b) cyclohexylidenecyclohexane; (c) the cyclohexane ring bearing adjacent $-\mathrm{COCl}$ groups; (d) the ring bearing adjacent $-\mathrm{CH(OH)CN}$ and $-\mathrm{COOH}$ groups; (e) $\mathrm{CH_3COCl}$ with anhydrous $\mathrm{AlCl_3}$.

Quick Tip to Solve: Reconstruct an alkene by joining the two ozonolysis carbonyl carbons; with thionyl chloride, replace each acid OH by Cl and retain the carbonyl oxygen and ring skeleton.

32(A)(a). Calculate the standard Gibbs energy ($\Delta_r G^\circ$) of the following reaction at 25 °C:

Au(s) + Ca^{2+}(1M) → Au^{3+}(1M) + Ca(s)

$E^\circ_{Au^{3+}/Au}$ = +1.5 V, $E^\circ_{Ca^{2+}/Ca}$ = -2.87 V

Predict whether the reaction will be spontaneous or not at 25 °C.

[1 F = 96500 C mol^{-1}] [3 marks]

Solution:

Concept:

- Standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- Standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred in the balanced reaction and $F = 96500\,\text{C mol}^{-1}$.
- A reaction is spontaneous under standard conditions if $\Delta_r G^\circ < 0$. Electrode potentials are intensive quantities and are not multiplied when half-reactions are scaled.

Step 1: Balance the electron transfer The printed equation specifies oxidation of gold and reduction of calcium ions. Balance these processes before using the Gibbs-energy relation:

$$\mathrm{Au(s)} \longrightarrow \mathrm{Au^{3+}(aq)} + 3\,\mathrm{e^-}$$
$$\mathrm{Ca^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ca(s)}.$$

Multiply the gold half-reaction by 2 and the calcium half-reaction by 3, giving

$$2\,\mathrm{Au(s)} + 3\,\mathrm{Ca^{2+}(aq)} \longrightarrow 2\,\mathrm{Au^{3+}(aq)} + 3\,\mathrm{Ca(s)}.$$

Thus $n = 6$. The Gibbs energy below refers to one mole of this balanced reaction; the printed skeleton equation cannot itself define a charge-balanced reaction with all coefficients equal to one.

Step 2: Find the standard potential and energy Calcium-ion reduction is the cathodic process in the direction asked, while gold oxidation is the anodic process. Hence

$$E^\circ_{\text{cell}} = (-2.87) - (+1.50) = -4.37\,\text{V}.$$

Quick Tip to Solve: Use the least common multiple of the two electron counts, 3 and 2, to get $n = 6$; never multiply either electrode potential by its balancing coefficient.

Substitute the balanced electron count:

$$\begin{aligned}\Delta_r G^\circ &= -6(96500)(-4.37)\\ &= +2530230\,\text{J mol}^{-1}\\ &= +2530.23\,\text{kJ mol}^{-1}.\end{aligned}$$

Here volt multiplied by coulomb gives joule. The positive sign means the reaction in the stated direction increases standard Gibbs energy at 25°C, so that direction is not spontaneous under the specified standard conditions.

Step 3: Conclusion For $2\,\text{Au} + 3\,\text{Ca}^{2+} \longrightarrow 2\,\text{Au}^{3+} + 3\,\text{Ca}$, $\boxed{\Delta_r G^\circ = +2.53023 \times 10^6\,\text{J mol}^{-1}}$. The reaction is non-spontaneous at 25°C under standard conditions.

Quick Tip to Solve: Use the least common multiple of the two electron counts, 3 and 2, to get $n = 6$; never multiply either electrode potential by its balancing coefficient.

32(A)(b). Tarnished silver contains Ag_2S. Can this tarnish be removed by placing tarnished silverware in an aluminium pan containing an inert electrolytic solution such as NaCl? The standard electrode potential for half reaction:

$\text{Ag}_2\text{S}\,(\text{s}) + 2\,\text{e}^- \longrightarrow 2\,\text{Ag}\,(\text{s}) + \text{S}^{2-}$ **is** -0.71 **V and for**

$\text{Al}^{3+} + 3\,\text{e}^- \longrightarrow 2\,\text{Al}\,(\text{s})$ **is** -1.66 **V.** [2 marks]

Solution:

Concept:

- Aluminium can supply electrons by oxidation, while silver sulphide can accept electrons to form metallic silver.
- For a proposed galvanic reaction, $E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{anode reduction}}$. A positive value gives $\Delta_r G^\circ < 0$.

Step 1: Identify the coupled half-reactions The tarnish is reduced according to

$$\text{Ag}_2\text{S}\,(\text{s}) + 2\,\text{e}^- \longrightarrow 2\,\text{Ag}\,(\text{s}) + \text{S}^{2-}(\text{aq}).$$

Aluminium is oxidised and supplies these electrons:

$$\text{Al}\,(\text{s}) \longrightarrow \text{Al}^{3+}(\text{aq}) + 3\,\text{e}^-.$$

The aluminium half-reaction printed in the question has an extra coefficient 2 before metallic aluminium. Atom and charge conservation require the balanced reduction half-reaction $\text{Al}^{3+} + 3\,\text{e}^- \longrightarrow \text{Al}$; its supplied reduction potential is used as -1.66 V.

Step 2: Test whether removal is spontaneous Using the given reduction potentials,

$$E^\circ_{\text{cell}} = -0.71 - (-1.66) = +0.95\,\text{V}.$$

Quick Tip to Solve: Keep both tabulated values as reduction potentials: subtract -1.66 V from -0.71 V, because aluminium is the metal being oxidised.

Balancing the two half-reactions gives

$$3\,Ag_2S\,(s) + 2\,Al\,(s) \longrightarrow 6\,Ag\,(s) + 3\,S^{2-}(aq) + 2\,Al^{3+}(aq).$$

The positive potential makes this reaction thermodynamically favourable. Metallic silver is restored as aluminium is consumed. The inert electrolyte permits ionic conduction, and electrical contact between the silverware and aluminium permits electron transfer; the salt need not act as the reducing agent.

Step 3: Conclusion Yes. With electrical contact in the electrolyte, aluminium reduces the Ag_2S tarnish to metallic silver because $\boxed{E^\circ_{\text{cell}} = +0.95\,\text{V}}$.

Quick Tip to Solve: Keep both tabulated values as reduction potentials: subtract $-1.66\,\text{V}$ from $-0.71\,\text{V}$, because aluminium is the metal being oxidised.

OR

32(B)(a). Define the following:

(i) Cell potential

(ii) Fuel cell [2 marks]

Solution:

Concept:

- An electrochemical cell develops a potential difference because its electrodes have different tendencies to undergo reduction.
- A fuel cell is a galvanic cell that converts the chemical energy of continuously supplied reactants directly into electrical energy.

Step 1: Define cell potential Cell potential is the potential difference between the cathode and the anode of an electrochemical cell. In terms of their reduction electrode potentials,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}.$$

It is measured in volts. When no current is drawn, this potential difference is the electromotive force (emf) of the cell. Under standard conditions it is denoted by E°_{cell}. A positive cell potential corresponds to a spontaneous galvanic reaction in the chosen direction.

Step 2: Define a fuel cell A fuel cell is a galvanic cell in which a fuel and an oxidant are supplied continuously to the electrodes and undergo electrochemical reactions to produce electricity. Products are removed so operation can continue while reactants are fed. For example, in a hydrogen-oxygen fuel cell, hydrogen is the fuel and oxygen is the oxidant, and the overall reaction is

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O\,(l).$$

The conversion is direct: the chemical reaction drives electron flow through an external circuit without first generating electricity from mechanical work.

Quick Tip to Solve: For cell potential state the electrode difference and unit; for a fuel cell include continuous reactant supply and direct conversion of chemical energy into electricity.

Step 3: Conclusion Cell potential is the cathode-to-anode potential difference. A fuel cell continuously converts the chemical energy of supplied fuel and oxidant into electrical energy.

Quick Tip to Solve: For cell potential state the electrode difference and unit; for a fuel cell include continuous reactant supply and direct conversion of chemical energy into electricity.

32(B)(b). Calculate emf of the following cell at 25 °C:
Zn(s) | Zn^{2+}(0.1 M) || Cd^{2+}(0.01 M) | Cd(s)
Given: $E^{\circ}_{Cd^{2+}/Cd}$ = -0.40 V, $E^{\circ}_{Zn^{2+}/Zn}$ = -0.76 V
[log 10 = 1] [3 marks]

Solution:

Concept:

- In cell notation the left electrode is the anode and the right electrode is the cathode; $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{right}} - E^{\circ}_{\text{left}}$.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, where n counts transferred electrons and Q is the reaction quotient.
- Pure solid metals have unit activity and are omitted from Q; dilute ionic activities are approximated by their molar concentrations.

Step 1: Write the cell reaction and standard emf Zinc is oxidised on the left and cadmium ions are reduced on the right:

$$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-}$$
$$\mathrm{Cd^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cd(s)}.$$

The overall reaction is

$$\mathrm{Zn(s)} + \mathrm{Cd^{2+}(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Cd(s)},$$

so $n = 2$. Using reduction potentials for both electrodes,

$$E^{\circ}_{\text{cell}} = (-0.40) - (-0.76) = +0.36\,\mathrm{V}.$$

The positive standard emf is consistent with zinc supplying electrons to the cadmium electrode.

Step 2: Apply the concentration correction The product ion is Zn^{2+}, and the reactant ion is Cd^{2+}. Hence the quotient for the reaction as written is

$$Q = \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cd^{2+}}]} = \frac{0.1}{0.01} = 10.$$

Quick Tip to Solve: For this cell, place the left-hand zinc-ion concentration over the right-hand cadmium-ion concentration in Q: $0.1/0.01 = 10$, and use $n = 2$.

Do not include either solid metal in this ratio. Substituting $\log 10 = 1$ into the Nernst equation gives

$$\begin{aligned} E_{\text{cell}} &= 0.36 - \frac{0.0591}{2} \log 10 \\ &= 0.36 - 0.02955 \\ &= 0.33045\,\text{V}. \end{aligned}$$

Because $Q > 1$, the concentration correction reduces the emf below its standard value. This sign check also confirms the quotient has been taken in the correct order.

Step 3: Conclusion The cell emf at 25°C is $\boxed{E_{\text{cell}} = 0.33045\,\text{V} \approx 0.330\,\text{V}}$.

Quick Tip to Solve: For this cell, place the left-hand zinc-ion concentration over the right-hand cadmium-ion concentration in Q: $0.1/0.01 = 10$, and use $n = 2$.

33(A). An organic compound 'A', molecular formula C_2H_6O oxidises with CrO_3 to form a compound 'B'. Compound 'B' on warming with iodine and aqueous solution of NaOH gives a yellow precipitate of compound 'C'. When compound 'A' is heated with conc. H_2SO_4 at 413 K gives a compound 'D', which on reaction with excess HI gives compound 'E'. Identify compounds 'A', 'B', 'C', 'D' and 'E' and write chemical equations involved. [5 marks]

Solution:

Concept:

- Controlled oxidation of a primary alcohol gives an aldehyde. The symbol $[O]$ represents an oxygen equivalent supplied by the oxidising agent.
- Ethanal gives the iodoform test: iodine and aqueous alkali convert its CH_3CO- unit into yellow CHI_3. The yellow solid is called iodoform.
- At $413\,\text{K}$, concentrated sulphuric acid causes intermolecular dehydration of ethanol to an ether. Excess hydrogen iodide cleaves the ether and also converts the initially formed alcohol into an alkyl iodide.

Step 1: Identify A and its oxidation product B A is ethanol, CH_3CH_2OH: its oxidation gives ethanal, B, CH_3CHO, which responds to the iodoform test:

$$CH_3CH_2OH + [O] \xrightarrow{CrO_3} CH_3CHO + H_2O.$$

The positive iodoform test identifies the aldehyde stage of oxidation. Dimethyl ether, the other C_2H_6O isomer, does not follow this alcohol oxidation and dehydration sequence.

Step 2: Identify the yellow precipitate C Ethanal contains the methyl carbonyl group. Warming it with iodine and aqueous sodium hydroxide gives yellow iodoform (triiodomethane), C, CHI_3, and sodium methanoate:

$$\begin{aligned} &CH_3CHO + 3I_2 + 4NaOH \\ &\longrightarrow CHI_3 \downarrow + HCOONa + 3NaI + 3H_2O. \end{aligned}$$

Step 3: Identify the dehydration product D Two ethanol molecules undergo intermolecular dehydra-

Quick Tip to Solve: Use the yellow iodoform precipitate to identify ethanal, then use 413 K to select ether formation; with excess HI, convert both ethyl groups of the ether into iodoethane.

tion at 413 K, giving D, ethoxyethane (diethyl ether):

$$2C_2H_5OH \xrightarrow[413\,K]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O.$$

At the stated 413 K, ether formation is favoured; ethene formation requires the higher dehydration temperature.

Step 4: Identify E after reaction with excess HI Hydrogen iodide first cleaves the ether to give iodoethane and ethanol. Because HI is in excess, the ethanol also reacts to give iodoethane:

$$C_2H_5OC_2H_5 + HI \longrightarrow C_2H_5I + C_2H_5OH,$$
$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O.$$

Adding the two stages gives the overall chemical equation:

$$C_2H_5OC_2H_5 + 2HI \longrightarrow 2C_2H_5I + H_2O.$$

E is therefore iodoethane (ethyl iodide), C_2H_5I. Excess HI converts the initially formed ethanol as well.

Step 5: Conclusion $A = CH_3CH_2OH$ (ethanol), $B = CH_3CHO$ (ethanal), $C = CHI_3$ (iodoform), $D = C_2H_5OC_2H_5$ (ethoxyethane) and $E = C_2H_5I$ (iodoethane).

Quick Tip to Solve: Use the yellow iodoform precipitate to identify ethanal, then use 413 K to select ether formation; with excess HI, convert both ethyl groups of the ether into iodoethane.

OR

33(B). (a) Write chemical equations of the following reactions:

(i) Phenol is treated with conc. HNO_3

(ii) Propene is treated with B_2H_6 followed by oxidation by H_2O_2/OH^-.

(iii) Sodium t-butoxide is treated with CH_3Cl.

(b) Give a simple chemical test to distinguish between butan-1-ol and butan-2-ol.

(c) Arrange the following in increasing order of acid strength:

phenol, ethanol, water [5 marks]

Solution:

Concept:

- The hydroxyl group activates the phenol ring and directs electrophilic substitution to the ortho and para positions. Concentrated nitric acid gives the trinitro derivative.
- Hydroboration followed by oxidation adds water across an alkene in the anti-Markovnikov orientation: the hydroxyl group appears at the less substituted carbon.
- Williamson ether synthesis couples an alkoxide ion with a suitable alkyl halide by nucleophilic substitution. A methyl halide cannot undergo competing beta-elimination.

Quick Tip to Solve: Put OH on the terminal carbon in hydroboration-oxidation; for the iodoform test, first look for the CH3CH(OH)- group in the alcohol.

- The iodoform test detects alcohols containing the $CH_3CH(OH)-$ group. Acid strength depends on the stability of the conjugate base formed after loss of H^+.

Step 1: (a)(i) Nitration of phenol On treatment with concentrated nitric acid, phenol forms 2,4,6-trinitrophenol, commonly called picric acid. Three ring hydrogen atoms, at positions 2, 4 and 6 relative to the hydroxyl group, are replaced by nitro groups:

$$C_6H_5OH + 3HNO_3 \xrightarrow{\text{conc.}} C_6H_2(NO_2)_3OH + 3H_2O.$$

This is extensive nitration; the mono-nitrophenols associated with dilute nitric acid are not the requested products.

Step 2: (a)(ii) Hydroboration and oxidation of propene Diborane supplies borane, which adds across the double bond with boron attached to the terminal carbon. Oxidation with alkaline hydrogen peroxide replaces the carbon-boron bond by a carbon-oxygen bond. The product is propan-1-ol, not propan-2-ol. Writing $R = CH_3CH_2CH_2$, the balanced stages are:

$$6CH_3CH{=}CH_2 + B_2H_6 \longrightarrow 2R_3B,$$
$$2R_3B + 6H_2O_2 \xrightarrow{OH^-} 6ROH + 2B(OH)_3.$$

Here $ROH = CH_3CH_2CH_2OH$. The equations show the usual boric-acid representation of the oxidation product; in alkaline solution it exists as borate.

Step 3: (a)(iii) Williamson synthesis using sodium tert-butoxide The tert-butoxide ion attacks the methyl carbon of chloromethane, displacing chloride and forming methyl tert-butyl ether (2-methoxy-2-methylpropane):

$$(CH_3)_3CONa + CH_3Cl \longrightarrow (CH_3)_3COCH_3 + NaCl.$$

Although tert-butoxide is bulky, the halide is methyl chloride, whose carbon is accessible for substitution and which has no beta-carbon for elimination.

Step 4: (b) Distinguish the alcohols by the iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Butan-2-ol gives a yellow precipitate of iodoform, CHI_3, whereas butan-1-ol gives no yellow precipitate. Butan-2-ol contains the required $CH_3CH(OH)-$ group and is oxidised to butan-2-one before haloform cleavage. Its overall equation is:

$$CH_3CH(OH)CH_2CH_3 + 4I_2 + 6NaOH$$
$$\longrightarrow CH_3CH_2COONa + CHI_3 + 5NaI + 5H_2O.$$

Butan-1-ol lacks that structural group and therefore does not undergo this characteristic reaction.

Step 5: (c) Compare the conjugate bases Phenol forms the phenoxide ion, whose negative charge is delocalised through resonance over oxygen and the aromatic ring. This stabilisation makes phenol appreciably more acidic than water and ethanol. Ethanol forms ethoxide; the electron-releasing ethyl group increases electron density on oxygen and destabilises its negative charge relative to hydroxide. Hence ethanol is less acidic than water. The increasing acid-strength order is therefore:

$$\boxed{\text{ethanol} < \text{water} < \text{phenol}}.$$

Quick Tip to Solve: Put OH on the terminal carbon in hydroboration-oxidation; for the iodoform test, first look for the CH3CH(OH)- group in the alcohol.

Step 6: Conclusion (a) The products are (i) 2,4,6-trinitrophenol (picric acid), (ii) propan-1-ol and (iii) methyl tert-butyl ether. (b) Butan-2-ol gives a yellow iodoform precipitate; butan-1-ol does not. (c) Increasing acid strength: ethanol $<$ water $<$ phenol.

Quick Tip to Solve: Put OH on the terminal carbon in hydroboration-oxidation; for the iodoform test, first look for the CH3CH(OH)- group in the alcohol.